THE INFLUENCE OF SELECTED SURFACTANTS AND WATER QUALITY PARAMETERS ON SURFACTANT-ENHANCED SOIL FLUSHING OF HYDROPHOBIC HYDROCARBON CONTAMINATED SOIL

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CONTAMINATED SOIL

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ABBREVIATIONS AND ACRONYMS

ATF	automatic transmission fluid
B	brine
BTEX	benzene, toluene, ethylbenzene and xylenes
CEC	cation exchange capacity
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act (aka Superfund)
Cells/ml	bacteria cells per milliter of solution
CM	centimeters
CMC	critical micelle concentration
CPM	counts per minute
DNAPL	denser-than-water non-aqueous phase liquid
EOR	enhanced oil recovery
EPA	United States Environmental Protection Agency
Ex situ	original position or site (excavated)
G	1 gravity force
Gal/min	gallons per minute
HPLC	high pressure liquid chromatography
HLB	hydrophile-lipophile balance
HOC	hydrophobic organic compounds

In situ	in place
ISSSF	*in situ* surfactant-enhanced soil flushing
$K_{o/w}$	octanol/water partition coefficient
L	liter
LNAPL	lighter-than-water non-aqueous phase liquid
NAPL	non-aqueous phase liquid
LSC	liquid scintillation counter
NTA	nitrilotriacetic acid
M	meter
ME or me	milliequivalents
MG or mg	milligram
MIN	minute
MSDS	material safety data sheets
OSHA	Occupational Health and Safety Administration (U.S. Department of Labor)
OUFS	operable unit feasibility study
PAH	polynuclear aromatic hydrocarbons
PCB	polychlorinated biphenyls
PCE	perchloroethylene
PCP	pentachlorophenol
pH	negative log of the hydrogen ion concentration
ppb	parts per billion
ppm	parts per million
RPM	revolutions per minute

S	surfactant
SARA	Superfund Amendment and Reorganization Act
SC	surfactant concentration
SDS	sodium dodecylsulfate
SITE	Superfund Innovative Technology Office
SSHP	site safety and health plan
Surfactant	surface active agent
TC	target compound
TCC	target compound concentration
TCE	trichloroethylene
TOC	total organic carbon
TOX	total organic halogens
T or TYPE	type of flushing solution (surfactant or water)
um	micrometers
USEPA	United State Environmental Protection Agency (or EPA)
UV	ultra-violet spectrophotometry

CHAPTER I

INTRODUCTION

Substances that have been dumped, leaked, or spilled into or on soil pose a potential contamination problem for surface and/or ground water. Contaminants that are hydrophobic organic compounds with high molecular weights pose a special hazard. They adsorb to soil and soil organic matter, and /or collect in the interstitial pores of the soil as they migrate through the soil column and aquifers to the bottom of the contaminated aquifer. Research and experience at contaminated sites indicate that residual hydrophobic organic contaminants slowly leach into ground water and contaminate the water at levels higher than drinking water standards (Cherry et al., 1990).

Remedial action undertaken to decontaminate contaminated sites can involve *in situ* or *ex situ* process systems. One of the most widely used *in situ* remedial action techniques has been the pump-and-treat system. This soil treatment process removes the contaminated surface or ground water for treatment via the appropriate unit operation either on or off site, and is quite effective for hydrophilic compounds. Pump-and-treat techniques do not, however, address the problem of residual hydrophobic organic compounds that have permeated the soil and/or aquifer and are immiscible in water. The residual immiscible compounds are trapped in the porous media and are not pumped out of the contaminated area with the conventional pump-

and-treat system as are the soluble contaminants. Thus the residual immiscible contaminants act as *in situ* long-term contamination sources. With time, the soil conditions (pH, temperature, water level, etc.) may change allowing the contaminants to leach into the groundwater. The pump and treat remedial action technique does not, therefore, provide permanent aquifer remediation when hydrophobic compounds are the partial or sole source of the soil/ground water contamination.

The projected length of time to remediate a multi-phase contaminated site, often greater than 30 years, and the lack of successfully remediated sites has prompted the establishment of the Superfund Innovative Technology Office (SITE) within the U.S. Environmental Protection Agency. The SITE office encourages research, development and implementation of innovative remediation techniques. *In situ* surfactant-enhanced soil flushing (ISSSF) is one such technique currently under development.

Chemical countermeasures can be taken which will increase the miscibility of the organics by reducing the surface tension at the interfaces of the soil, water,and organic system. Surface active agents (surfactants) are long chain hydrocarbons which possess a polar or ionic head moiety and a hydrophobic hydrocarbon chain portion. The polar head group interacts with water while the hydrocarbon portion reacts very weakly with water but is soluble in organic compounds. The surfactant molecule thus partitions between the two phases. In this way, the surfactants reduce the surface tension at the water-organic interface allowing the hydrophobic compound to become more water soluble and/or mobile.

Surfactants have been used for many years in the oil producing industry for enhanced oil recovery (EOR) of residual oil trapped in porous media. Surfactant solutions pumped down hole reduce the surface tension of the trapped residual oil, hence its adsorption to geologic material, rendering the oil less viscous. When subsequent water or steam flooding of the oil reservoir occurs, the residual oil is more soluble, less viscous, more mobile, and amenable for pumping to the surface.

The investigation reported in this dissertation transferred the technology for enhanced oil recovery from the oil industry to *in situ* hazardous waste remediation of soil containing hydrophobic substances. Using laboratory shaker methods, this study investigated the influence of the ground water parameters, pH and brine at three concentration levels each, on the effectiveness of soil flushing with surfactants. Three different surfactants at three concentrations each were used in the study. Three concentration levels of three target compounds (hexadecane, o-cresol and phenanthrene) representing the aliphatic, alkyl aromatic and polynuclear aromatic hydrocarbon groups, respectively, were used.

The null hypotheses addressed in this study are as follows:

1. There are no differences between the levels of the following main effect variables in terms of mg of target compound desorbed from the soil with the surfactant flushing solution: a) surfactant, b) surfactant concentration, c) target compound, d) target compound concentration, e) pH and f) brine.
2. Using each surfactant, there are no differences between target compounds in terms of mg of target compound desorbed from the soil.

3. For each surfactant, there are no differences between target compound concentrations in terms of mg of target compound desorbed from the soil.
4. For each target compound, there are no differences between target compound concentrations in terms of mg of target compound desorbed from the soil.
5. For each surfactant concentration there are no differences between target compounds, in terms of the mg of target compound desorbed from the soil.
6. The pH level of the flushing solution for all surfactant types or for all target compounds or for all target compound concentrations does not make a difference in terms of the mg of target compound flushed from the soil.
7. The brine concentration of the flushing solution across surfactant type or for all target compounds or for all target compound concentrations does not make a difference in terms of the amount of target compound desorbed from the soil.
8. There are no differences between the water alone flushes and the surfactant flushes for brine, target compound, target compound concentration or pH.

CHAPTER II

OVERVIEW OF *IN SITU* SURFACTANT-ENHANCED SOIL FLUSHING

Introduction

Contaminated soils and aquifers are frequently remediated with the well known pump-and-treat (p-t) technique. Pumping the contaminated ground water from the site for treatment to remove and/or recover the contaminant is a feasible technique for soluble compounds. Soil flushing, application of water to *in situ* contaminated vadose zone soils, enhances the mobilization and transport of the contaminants to the ground water for pumping. However, many of the thousands of compounds that compose petroleum hydrocarbons are only slightly soluble in water or are hydrophobic.

Hydrophobic Organic Compounds or Non Aqueous Phase Liquids

Hydrophobic Organic Compounds (HOCs), or Non-Aqueous Phase Liquids (NAPLs), have high octanol/water partition coefficients (K_{ow}). The K_{ow} has been demonstrated to be inversely proportional to the solubility of a compound (Chiou and Freed, 1977; Chiou, 1982); NAPLs are thus immiscible in water. NAPLs may take several forms in a multi-phasic soil-air-water-contaminant system (Figure 1, Page 7). As contaminants migrate downward in the subsurface, their interactions with the soil

matrix induce phase changes. Volatile contaminants can be found in the vapor phase in the air trapped in the vadose zone. The contaminants may adsorb onto organic matter and/or the solid soil phase. Soil water and/or ground water may contain contaminants up to the levels of their solubility. Also, the NAPLs may be trapped as ganglia in interstitial pores by capillary forces or collected in pools.

When the migrating NAPLs meet barriers, they are likely to spread laterally and form pools (Figure 2, Page 7). NAPLs are divided into two common categories, light and dense. Lighter-than-water Non-Aqueous Phase Liquids (LNAPLs) may form pools at barriers in the vadose zone and/or float on the water table. Denser-than-water Non-Aqueous Phase Liquids (DNAPLs) sink to the bottom of the aquifer by gravity and form free product pools at the aquitard.

For immiscible hydrocarbons, traditional pump-and-treat remedial action systems are ineffective and leave residual DNAPLs (Abdul et al., 1990; Cherry et al., 1990; Haley et al., 1991; Johnson et al., 1991; Olsen and Kavanaugh, 1993). The residual DNAPLs may slowly solubilize and pose a long-term threat to the quality of the affected ground water and human health (West, 1991). DNAPLs exist at numerous hazardous waste sites, are largely undetected and are likely to be a significant limiting factor in site remediation (Huling and Weaver, 1991). Although DNAPL solvents are immiscible in water and have relatively low solubilities in water (typically 100 to 5000 mg/l), their solubilities are often many orders of magnitude higher than their respective drinking water standards (Cherry et al., 1990). Remediation of NAPLs in soil-water systems is often dependent on desorption of the

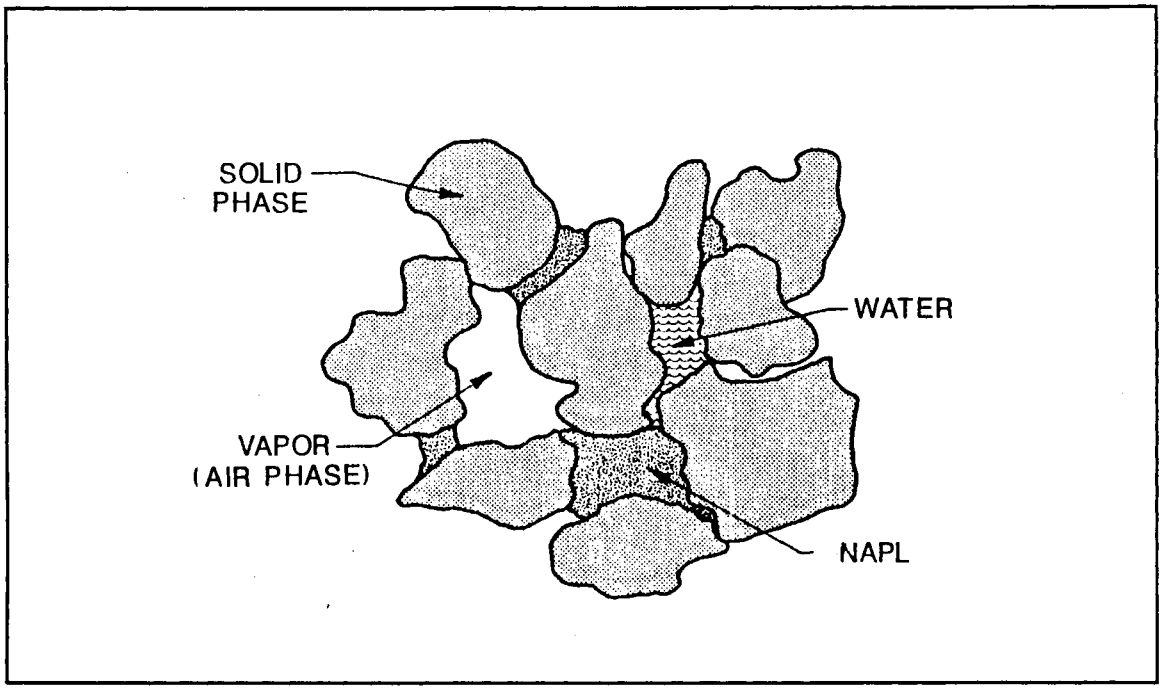

Figure 1. Four Phases of a NAPL Contaminant in the Vadose Zone (Kimball, in press, with permission)

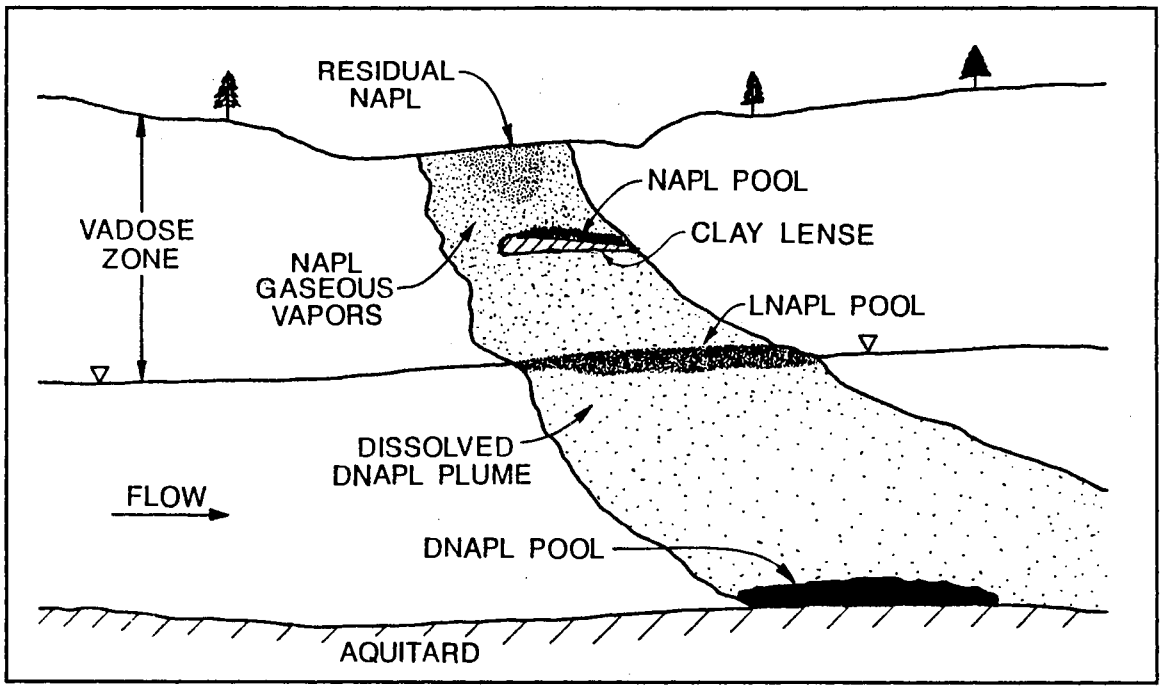

Figure 2. Possible NAPL Distribution in a Contaminated Geoenvironment (Kimball, in press, with permission)

contaminant from the soil surface and subsequent incorporation of the pollutant into the bulk aqueous phase for remedial treatment (Edwards et al., 1991).

Surfactants

Surfactants are amphiphilic molecules with a hydrophobic (hydrocarbon or fluorocarbon) chain moiety and a hydrophilic (polar or ionic) head group (Figure 3, Page 9). The amphiphilic nature of a surfactant molecule enables it to exist in one or more forms in a biphasic or multiphasic system: dissolved in water as a monomer, adsorbed at an interface, or incorporated with other surfactant molecules as part of a micelle (Edwards et al., 1991).

Micelles (Figure 4, Page 9) are formed at the Critical Micelle Concentration (CMC) which is the aqueous surfactant concentration at which surfactant monomers form colloidal aggregates. Surfactant chemistry, temperature, ionic strength, and the presence and type of organic additives determine the CMC (Rosen, 1989). At the CMC, abrupt changes in solution properties, such as surface tension, occur thus increasing the solubility of hydrophobic organics in water.

The unique properties of surfactants give them potential in remedial systems for petroleum contaminated soils. Surfactants may partition between or adsorb to the interfaces of an oil-water-soil system and reduce the interfacial tension. The polar head group interacts strongly with the water phase and the nonpolar hydrocarbon chain portion interacts very weakly with water molecules but partitions into HOCs.

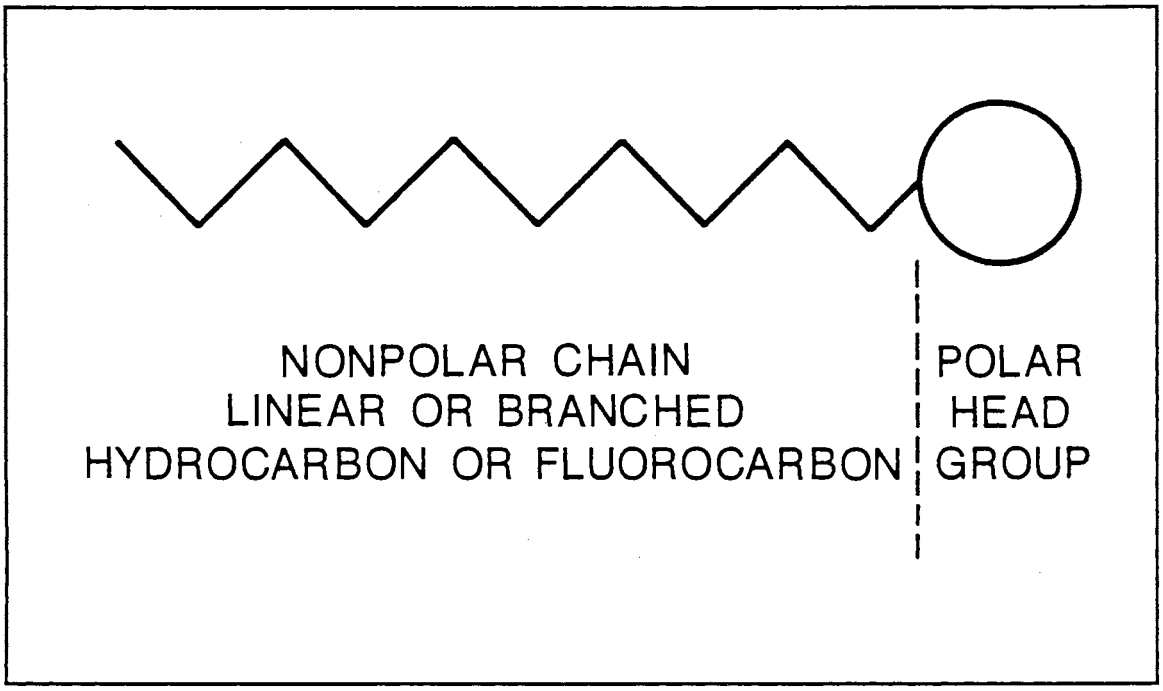

Figure 3. Basic Structure of a Surfactant Molecule (Kimball, 1992, with permission)

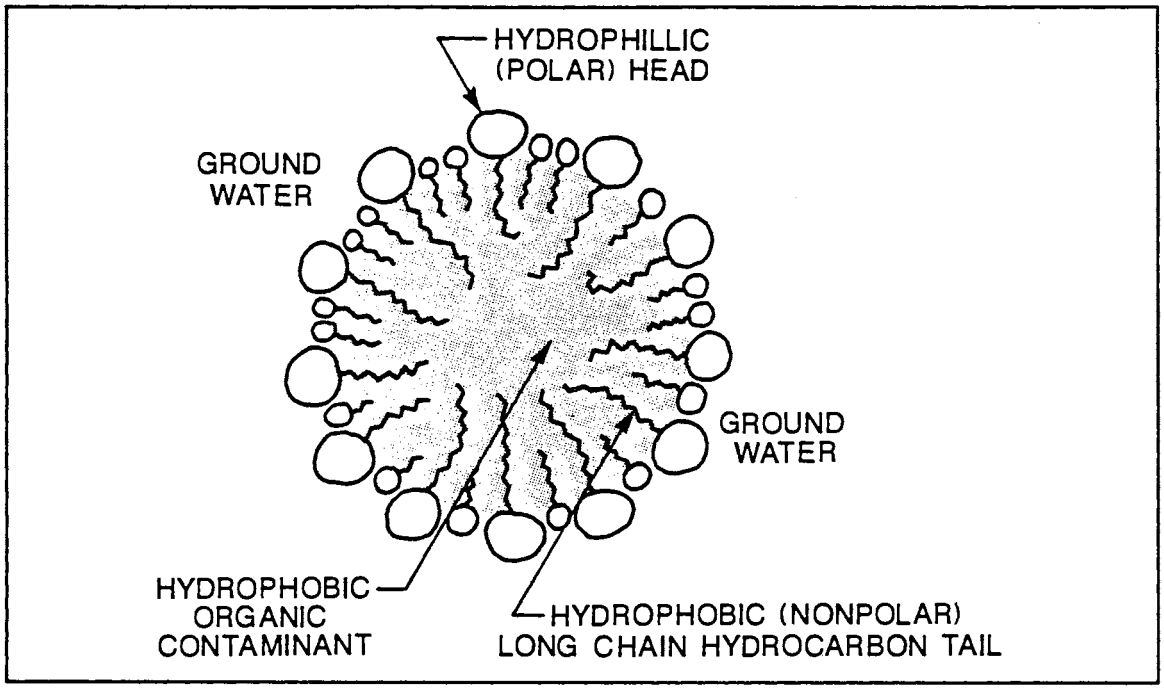

Figure 4. Micelle in Contaminated Ground Water (Kimball, 1992, with permission)

The hydrophobic organic contaminants are thus desorbed from the soil, solubilized and/or mobilized allowing the implementation of pump-and-treat remediation after soil exposure to the surfactant(s) solution.

Surfactants are classified according to the nature of the hydrophilic head group (Rosen, 1978). Anionic surfactants have a negatively charged head group. Cationic surfactants have a positively charged head group. If both positive and negative charges are present in the surface-active head group the surfactant is known as zwitterionic. When there is no apparent ionic charge in the head group the surfactant is nonionic.

There are over 13,000 surfactants available (Christian et al., 1991). The selection of the most effective surfactant for a particular purpose is a function of the physical-chemical characteristics of the surfactant, the compounds of interest, and the environment of the multiphase system. For remediation of petroleum contaminated sites, therefore, the selection of the most effective surfactant(s) is highly site specific. Some investigators feel that surfactants represent a potentially powerful tool for the restoration of ground water sources if their effectiveness in a given application can be established (Vigon and Rubin, 1989). Vigon and Rubin have outlined guidelines for surfactant selection and dosage optimization for use in remediating contaminated aquifers. Unsuitable surfactants can cause soil dispersion and pore clogging.

EOR Technology Transfer

Because they reduce viscosity, surfactants have long been used by many segments of the oil industry in various products and processes: motor oil additives, oil

dispersants, machinery degreasers, drilling muds and EOR. EOR systems are tertiary oil recovery systems designed to capture a portion of the 65 to 70% of the original oil-in-place that is left in the reservoirs at the end of waterflooding (Shah, 1981). Viscous and capillary forces trap the discontinuous oil ganglia in the pores of the reservoir media. Surfactant-enhanced oil recovery is a chemical process that injects surfactants, or bacteria that produce biosurfactants, into the oil reservoir (Bryant, 1987). The surfactants lower the interfacial tension of the oil-porous media system, hence reducing the oil viscosity and the capillary forces that have trapped the oil. When the reservoir is flooded, the displaced oil is more mobile, due to the reduced surface tension, and is pumped to the surface for recovery.

Transferring the technology from EOR to soil remediation, *In Situ* Surfactant-enhanced Soil Flushing (ISSSF) has recently been applied to the remediation of petroleum contaminants in the vadose zone and/or saturated zone soils as well as in ground water. Although the literature on secondary recovery of petroleum products has helped to define the complexity of enhanced recovery processes, the understanding and technology developed to address that problem cannot be adopted without modifications for the *in situ* cleanup of soil and ground water contamination (Abdul et al., 1990). Differences in the nature and composition of the geologic matrices of the two types of systems relate to the behavior of the interactions of the phases. Modifications to accomodate the soil matrix components must be made to apply surfactant flushing to contaminated soil.

ISSSF addresses the problem of removing HOC or NAPL residuals by desorption from soils, solubilizing, emulsifying and/or otherwise mobilizing the

hydrocarbon contaminants in water thus rendering the soil amenable to pump-and-treat remediation. ISSSF involves applying surfactant-water mixtures to contaminated soil, mobilizing the contaminants to the aquifer for removal via pumping to the surface for treatment. Figure 5, illustrates a proposed ISSSF pump-and-treat system designed by Oma et al. for Eckenfelder, Inc. with capability for surface and subsurface application of the surfactant (sodium dodecylsulfate) solution.

Application of Surfactants to Remedial Action

Background

The literature reports a limited number of published applications of surfactant-enhanced soil flushing. Interest in ISSSF has increased in the last few years, chiefly

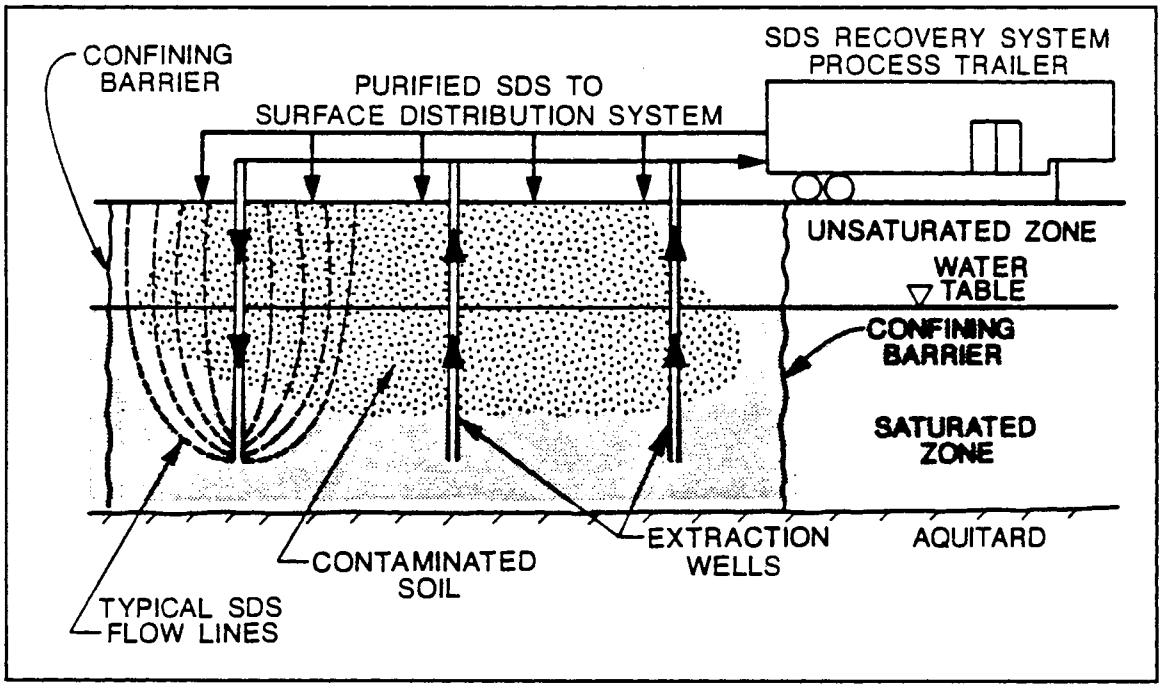

Figure 5. *In Situ* Surfactant-Enhanced Soil Flushing System Design (Oma et al., 1991, with permission)

in response to public demand for more rapid remediation at sites and EPA funding laboratory, field and modeling studies. However, many of the funded studies have not completed data collection or the data are proprietary; hence the results are not published.

Initial studies investigating the use of surfactant solutions for flushing petroleum products from contaminated soils were conducted by the American Petroleum Institute (API, 1979 and 1985). Ellis and Payne (1983) performed the initial investigation and laboratory research for using ISSSF as a remediation technique for general hazardous waste contamination. Their report to the U.S. Environmental Protection Agency (USEPA) Chemical Countermeasures Program of the Oil and Hazardous Materials Spills Branch presented the results of an information search on uncontrolled hazardous chemical spills and waste disposal sites and subsequent laboratory studies.

The Chemical Countermeasures Program's purpose was to investigate and report on *in situ* methods for remedial action at hazardous waste/spill sites. The program was to "provide guidance and define techniques so that the use of a chemical countermeasure minimizes the overall harm to human health and the environment and does not worsen the environmental impact" (Ellis and Payne, 1983).

Based on the information search, laboratory research using ISSSF was conducted on three categories of hazardous waste: phenols, metals, and crude oil. Laboratory shaker table and column studies were conducted on Freehold soil contaminated with three pollutant groups; distilled Murban crude oil (containing polynuclear aromatic hydrocarbons and intermediate to high molecular weight

aliphatic hydrocarbons), chlorophenols and PCB mixtures in cholorbenzenes. Water flushing alone decontaminated the chlorophenols (0.5% residual), but was not successful with the Murban crude oil (90.6% residual) or the PCB mixture (80-90% residual). However, surfactant-enhanced flushing of the soil efficiently removed the test hydrophobic compounds (Murban crude oil and PCB mixture) from the soil with residuals of 7.0% and 2.0%, respectively. A mixture of nonionic surfactants, 2% Witco Adsee 799 and 2% Hyonic NP90, was used. The resulting reports recommended *in situ* surfactant-enhanced pump and treat remediation for slightly soluble and hydrophobic contaminants (Ellis and Payne, 1983; Ellis et al., 1985).

Site-Specific Characteristics

As with most remedial action techniques, the applicability and effectiveness of the system are contingent on the characteristics of the contaminated site. Decisions to utilize ISSSF must be made on a case by case basis and require site-specific evaluation and design. For the most efficient results, the following system variables should be carefully assessed and optimized.

Contaminant Type

As noted previously, hydrophobic (nonpolar, high K_{ow}) or slightly soluble organic contaminants which are immiscible in water will be best remediated with ISSSF. Polynuclear aromatic hydrocarbons (PAHs), creosol, polychlorinated biphenyls (PCBs), long chain aliphatic hydrocarbons and other heavy molecular weight organic compounds are good examples of these contaminant types. These

compounds have low mobility and a high environmental persistence in soil. Polar contaminants are amenable to pump-and-treat remediation systems alone as they readily solubilize and flush from the soil.

Soil Physical-Chemical Characteristics

Each site has unique characteristics and properties that will effect the type and performance of remedial system(s) used (Miller, in press). Thorough site characterization should precede field implementation (Mercer et al., in press).

Previous studies have indicated that the amount of organic carbon in the soil has a direct effect on the amount of contaminant adsorption (Karickhoff, 1981). For optimum results, therefore, organic carbon content of the site soil should be 2.0% or less. Soil organic carbon can adsorb organic contaminants, retard their movement in soil and flow in ground water and inhibit the surfactant action. Also, high soil organic carbon amounts may cause adsorption of the surfactant to the soil organic matter thus limiting the effectiveness of the surfactant by removing it from the system dynamics. Additional surfactant solution, hence additional cost, would thus be required for the remediation of the soil.

Grain size distribution of the soil is an important variable affecting ISSSF efficiency. The proportion of clay and silt-sized particles in soil directly influences the soil's capacity to adsorb and retain organic substances (Hillel, 1982). Mineralogic clay has low hydraulic conductivity and charged particles with a large surface area. Low hydraulic conductivity relates to small soil pores which retard the flushing action and surfactant solution-contaminant interaction. Also, small pores are easily clogged,

reducing flushing action. Charged clay particles adsorb some surfactants removing them from system dynamics. All of these characteristics reduce the effectiveness of ISSSF. Hence, clay and silt content of the site soil should be low, 10 - 15%. Moderate to high permeability (10^{-4} cm/sec or higher) is recommended (Ellis et al., 1985).

Extent of Contamination

ISSSF is ideal for sites where the contaminant is too deep or inaccessible for excavation. Ellis and Payne (1983) recommend ISSSF application at sites with contaminant migration depths of 2 to 30 feet below the surface. Removal of the contaminant source is the primary step in site remediation to avoid further contamination and contaminant migration. The site must have a geologic or artificial barrier below the contamination to prevent further vertical contaminant migration. The ideal areal extent of contamination for remediation has yet to be determined. Test cells have been limited to 1 acre or less to closely control variables, monitor test results and assure soil homogeneity (Nash and Traver, 1989; Sale and Pitts, 1989).

Age of contamination seems to have little influence on the effectiveness of test systems. Although the concentration of the contaminates in test systems has varied, resource recovery from long-standing saturated systems has been achieved (Gee et al., 1990: Sale and Pitts, 1989).

Implementation of *In situ* Surfactant-Enhanced Soil Flushing

Equipment

The ISSSF system on site is a basic pump-and-treat (p-t) system adapted with components to accommodate surfactant solution preparation, distribution and treatment. An ISSSF system can be broken down into the following segments:

* surfactant solution mixing and holding system
* surfactant distribution system
* recovery drains or contaminant capture system
* pumping systems for surfactant delivery and contaminant capture
* plume containment barriers
* recovered fluids treatment system

Surfactant mixing and holding can be implemented with conventional water treatment mixing and holding tanks. Surfactant solution delivery systems include surface sprinklers or injection wells. Irrigation piping and sprayers can control application of the solution to the soil surface. Conventional p-t piping and injection wells and/or horizontal wells can be utilized to deliver the surfactant solution to the subsurface environment up gradient of the plume.

Perforated recovery wells, French drain systems, or interceptor trenches can be utilized to capture the contaminated ground water. The recovery system is placed down-gradient of the plume at several locations.

Conventional p-t surface or subsurface pumps are appropriate. The pumps should be sized for the hydrogeologic conditions of the site.

Plume contaminant barriers prevent off site migration of the contaminants and should extend to bedrock. They can take several forms. Sheet pilings are useful to limited depths. Slurry walls have been used at numerous sites. Hydraulic barriers could be established by using off site injection wells to control hydraulic flow. If there is no horizontal barrier (bedrock or other aquitard) at a convenient depth, one may have to be established with horizontal drilling and filling or grouting.

Recovered fluids can be treated on or off site. The recovered fluids treatment system utilizes the same type of equipment as conventional ground water and surface water treatment systems (air stripping, carbon adsorption, filtration, separation processes, biodegradation, etc.). For sites with a mixture of contaminants, combinations of systems may be needed.

Figure 6 illustrates a pilot test system for the treatment of soils contaminated with wood treatment products and the recovery of the contaminants (PCP and creosote). Sodium dodecylsulfate was used as the flushing surfactant.

Preliminary Laboratory Studies

Most system parameters can be defined with laboratory investigations and bench scale studies. Thorough site characterization includes the following:

* contaminant identification, concentration gradient range and location

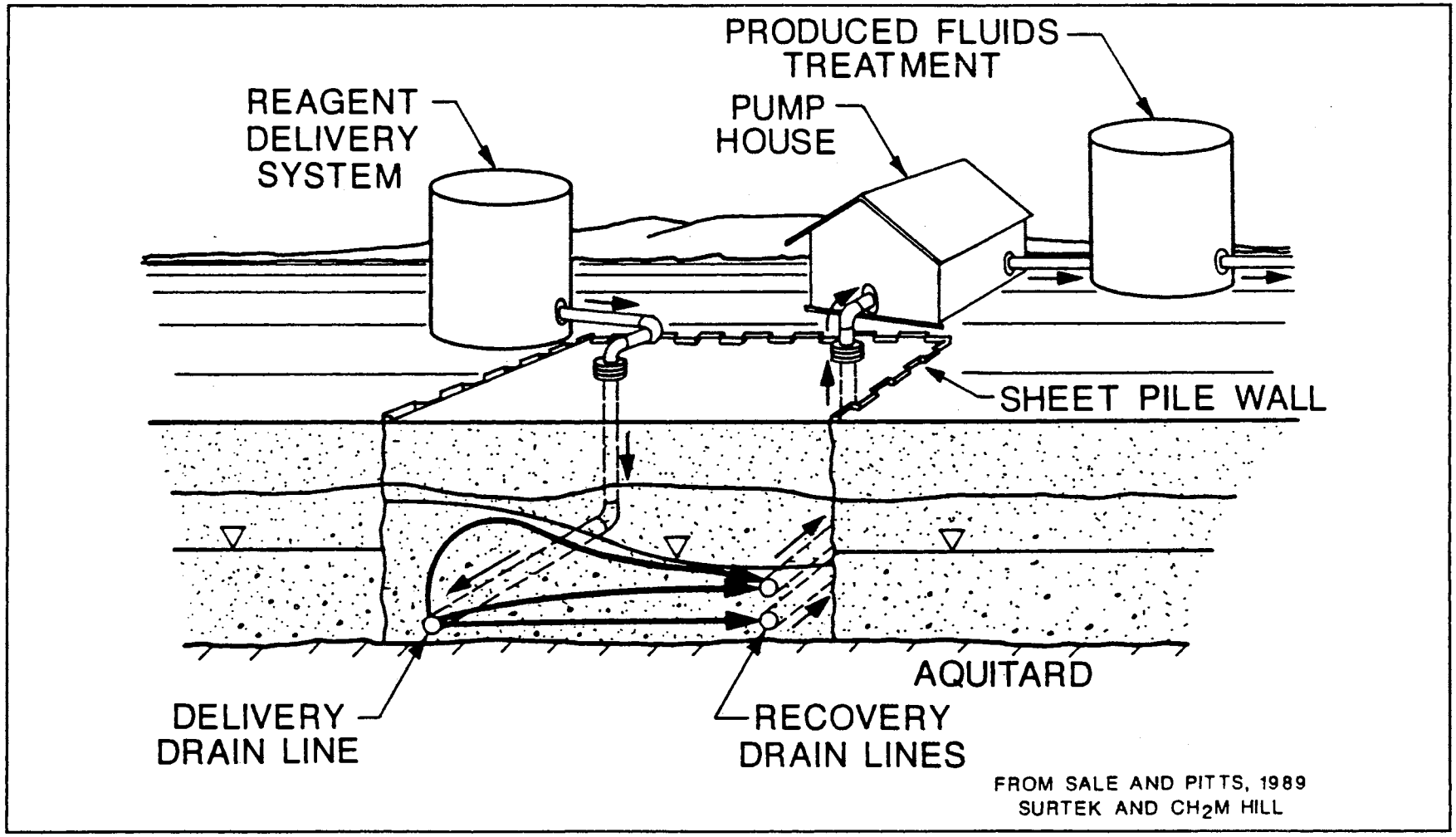

Figure 6. Pilot Study Pump-and-Treat System Design with Modifications for Surfactant Enhancement (Sale and Pitts, 1989, with permission)

* soil characterization
* hydrologic characterization
* geologic characterization

Shaker table and soil column bench studies that simulate field conditions help predict the interactions of the soil, ground water and contaminant-flushing solution to be expected at a specific site. Appropriate surfactant type and dosage can be determined with laboratory studies, as mentioned earlier (Vigon and Rubin, 1989). Injection and extraction pumping rates, operation time frame, and recovered flushing solution treatment systems can be determined in the laboratory as well.

The results of these lab studies are only an estimate, however, they can be extrapolated to expected field results under similar conditions. As with most lab studies, the results serve only as guidelines for field behavior. In one case, the field experiments did not conform to the prediction of the laboratory results (Nash et al., 1987). Non-homogeneous soil conditions in the field were thought to be the major differences between the lab and field results of that study. Site specific lab studies can be, however, valuable tools for designing an ISSSF remedial system.

Economics

Because of the site specific nature of remedial techniques in general and the limited field application of ISSSF in particular, it is difficult to obtain comprehensive, detailed cost estimates of this technique at this time. Also, much of the information produced by work that has been done in this area is proprietary. Over 40 letters were sent to companies listed in the Summer 1992 issue of Soils as having expertise

in ISSSF. The letters requested information of the companies' involvement with ISSSF systems, associated economic and site remediation data. Of the 11 responses, only 5 claimed expertise in this area. One of the 5 was a software data base company. One had expertise but no experience. Two had experience, but information was confidential. Only 1 company would share information on systems operated.

ISSSF systems are essentially pump-and-treat systems with the addition of a containment barrier around the site and surfactant solution mixing, holding and application systems. Hence, general economic comparisons can be made to p-t systems with allowances for the above mentioned additions. *In situ* soil flushing without surfactants is estimated to reduce subsurface remedial costs by at least ninety percent over other methods involving excavation, treatment and/or disposal (Gee et al., 1990).

Mathematical Modeling of Surfactant Flushing

The following preliminary economic evaluation of the technique was based on a process that was developed by Eckenfelder Inc., Nashville, Tennessee (Oma et al., 1991; Wilson and Clarke, 1991). The estimates were based on the results of two types of mathematical models of hypothetical contamination sites and represent the upper and lower estimates of remediation of an area with the characteristics and input parameters listed in Tables 1 and 2 , respectively.

TABLE 1

PARAMETERS AND VALUES OF MODELED SITE

Characteristic	Value
Area	1 Acre
Contaminant # 1	Aroclor 1254 in oil
Concentration (mg/kg)	Vadose Zone = 2,000 Saturation Zone = 200
Contaminant # 2	TCE
Concentration (mg/kg)	Vadose Zone = 200 Saturation Zone = 20
Vadose Zone Thickness	3 m (10 ft)
Aquifer Thickness	3 m (10 ft)
Soil Density	1700 kg/m^3
Soil Porosity	0.3
Surfactant	Sodium Dodecylsulfate
Concentration	2.6 % (25 kg/m^3)
Treatment Period	2 Years

TABLE 2

INPUT PARAMETERS FOR TWO COMPONENT
LOCAL EQUILIBRIUM MODEL

Parameter	Units
Aquifer Thickness	Meters
Length of Domain of Interest	Meters
Width of Domain of Interest	Meters
Injection Well Flow Rate	Gal/Min
Coordinates of Injection Well	X,Y
Recovery Well Flow Rate	Gal./Min
Coordinates of Recovery Well	X, Y
Influent Surfactant Concentration	Kg/Cubic Meters
Natural Ground Water Velocity	V_X, V_Y
Water-Filled Porosity of Aquifer	
Langmuir Parameter (A Capacity Factor)	$C_{a\ max}$
Langmuir Parameter (Strength of Adsorptive Binding)	$C_{1/2}$
Saturation Concentration of Contaminant in Pure Water	
SDS Critical Micelle Concentration	Mg/L
Slope of a Plot of Contaminant Concentration Versus Surfactant Concentration	
Total Contaminant Concentration	Mg/Kg
Coordinates of Lower Left Corner of Zone of Contamination	X, Y
Coordinates of Upper Right Corner of Zone of Contamination	X, Y

The best case model (Equilibrium Solubility Model) is a materials balance model based on the solubility limit of the organic contaminant(s) within the SDS surfactant. This model calculates the volume of surfactant needed to solubilize a givenmass of contaminants within the soil. The surfactant was distributed at the surface. The model predicted a cost estimate of $79.30 / cubic yard of contaminated soil.

The worst case estimate was made with the Two Component Local Equilibrium Model created by Wilson and Clarke, 1991. With this model, an injection and a recovery well flushed a 2-dimensional aquifer with surfactant solution. With a surfactant flow rate of 516 gal/min, this model predicts recovery of 95% of the PCB and all the trichloroethylene (TCE) in 2 years. Cleanup times depend on site specific soil and/or contaminant characteristics. This model gave an estimated remedial cost of $164.30/ cubic yard of contaminated soil.

The cost evaluation breakdown for both models is given in Table 3. The cost for ISSSF was considerable less than other forms of remediation. Oma et al., 1991, gave costs of $1,000 to $2,000 per cubic yard for incineration and $250 to $350 per cubic yard for off site disposal.

Capital Costs

Direct capital costs included purchased equipment, equipment installation, instrumentation and controls, piping, and electrical. A 12 percent interest rate and 7 year amortization were applied to capital costs. Indirect capital costs include engineering and supervision, construction expenses, fees, and contingency.

TABLE 3

COST EVALUATION BREAKDOWN FOR *IN SITU* SURFACTANT SOIL FLUSHING OF ONE ACRE EXAMPLE SITE

Cost Component	Equilibrium Solubility Model (78 gal/min SDS)		Two Component Local Equilibrium Model (516 gal/min SDS)	
	Total Cost ($1,000)	Unit Cost ($/cu yd)	Total Cost ($1,000)	Unit Cost ($/cu yd)
Amortized Cap. Equip.	978	30.40	3,039	94.40
Site Construction[a]	129	4.00	129	4.00
Operations & Main.				
Labor	727	22.60	915	28.40
Materials	414	12.60	414	12.80
Elect. Power	132	4.10	622	19.30
Analytical	31	1.00	31	1.00
Waste Disposal	143	4.40	143	4.40
TOTAL	2,554	79.30	5,293	164.30

[a] Site construction cost includes labor and materials.
[b] Site construction cost range is for excavation of PCB-contaminated soil without (lower cost) and with (higher cost) the use of sheet piling.

Operations and Maintenance Costs

Included in the operation and maintenance (O & M) costs were labor, materials, electrical power, analytical work, and waste disposal. The O & M costs comprised 56.6 % of the estimated total remediation cost.

Other Costs

Several site specific costs were not included in the economics of the remediation evaluation.

* Remedial Investigation/Feasibility Study
* Permitting - Local, State, and Federal
* Oversite - Administrative and Legal Project Management
* Contractor Profit
* Contingency - Usually 10-15% of Total Cost

The above costs were excluded from the economic evaluation because they vary considerably from site to site and are basic to any remedial action.

Estimates from Bench Scale Study

A bench scale study conducted for a truck maintenance superfund site in 1992 provided data for estimations of full-scale *in situ* surfactant-enhanced soil flushing systems for similar sites (Harper, 1993). The target contaminants included high concentrations of polynuclear aromatic hydrocarbons (PAHs), volatile organics, and low concentrations of heavy metals. Soil columns of the sandy silt contaminated soil from the site were flushed for 22 days with solutions of Triton X-100 and

nitrilotriacetic acid (NTA). Levels of 59% to 85% removal of the semivolatile PAH target compounds were achieved. Based on this and similar studies, cost estimates of $45 to $85 per ton of soil were predicted for a full-scale *in situ* soil flushing treatment system. Treatment of the flushing solution was not included in the estimate.

General System Comparisons

Because of the site specific characteristics that are considerations in remedial system design, overall cost estimates are difficult to assess. With the increase in numbers of sites remediated, however, estimates are more realistic and reliable. Table 4 gives estimates for a number of remediation types for comparison with ISSSF. Not all site operations were included in the summary cost estimates; therefore, across the board comparisons cannot be made.

Case Histories

Typically, a section on case histories would be replete with cases illustrating the application of the technique in a variety of settings. However, since ISSSF is a relatively new technology, the number of actual reported and/or published cases is relatively low. There are, however, several important laboratory experiments which delineate basic research in this area. Laboratory studies are useful in determining influential parameters involved in developing effective surfactant-enhanced soil flushing systems (West, 1991). Thus, this section will review selected field case histories and laboratory studies. Table 5 presents data of the variables involved in the studies.

TABLE 4

REMEDIAL SYSTEMS - ECONOMIC COMPARISONS

System Type	$ /Cubic Yard	Reference
ISSSF	164.30	Oma et al.
ISSSF	45-85/ ton	Harper
ISSSF	$3-5,000/well flushing fluid-$10,000/mo + recovery fluid treatment	Johnson et al., p 14-2
Soil Washing	120/ton + wash fluid treatment	Johnson et al., p 15-3
Incineration	1-2,000	Oma et al.
Incineration	1,000/ton median 1,500-2,000/ton highly toxic	Long et al., p 35
Incineration	150-300/ton - large facilities 150-800/ton -turnkey facilities	Johnson et al., p 8-3
Soil Vapor Extraction	60/cu yd including recovered air treatment	Long et al., p 22
Soil Venting	3-5,000/ well 5-10,000 pipe & misc. 1-5,000 utilities/mo blower/vacuum pump 1-5,000 vapor treatment system 75- 120,000/mo lease pump & vapor treatment system - 12,000/mo	Johnson et al., p 13-3
Thermal Desorption	Lower than incineration but higher than *in situ*	Long et al., p 36
Thermal Desorption	100/ton	Johnson et al., p 9-2
Land Treatment	70 - 120	Long et al., p 29
Land Treatment	5-50 for sites over 1500 cu yds	Johnson et al., p 4-2
In Situ Bioremediation	100-200	Long et al., p 31

TABLE 4 (Continued)

System Type	$ /Cubic Yard	Reference
In Situ Bioremediation	100-300,000 / site for 1-3 years (O & M and Capital)	Johnson et al., p 7-3
Bioreactor	100-200 High O & M Costs Capital Intensive	Long et al., p 26
Landfill	200-300/ ton	Johnson et al., p 5-2
Landfill	250-350/ cu yd	Oma et al.
Compost	60-150/ton	Johnson et al., p 5-2

TABLE 5

FIELD STUDIES DATA

	Sale and Pitts (1989)	Nash et al. (1987)
Contaminant	Pentachlorophenol Creosote (93,000 mg/kg total)	Chloroform (130 ug/l) TCA (39 ug/l) TCE (100 ug/l) Toluene (36,000 ug/l) Benzene (31,000 ug/l) Ethyl Benzene (6,800 ug/l) Oil and Grease (1050-5,800 mg/kg)
Site Characteristics	12 ft Alluvial Aquifer Underlain by Shale	95% Sand, 5% Finer than Sand (Boone Fine Sand) for 10-15 ft; Underlain by Weathered Sandstone
Flushing Solutions	Makon 10 (Stepan Chem. Co.) Polystep A7 Xanthan Gum Biopolymer 0.1 - 0.825 % by wt Na_2CO_3 or Na_2HCO_3	Ethoxylated Fatty Acids (Witco) Ethoxylated Alkyl Phenol(Diamond Shamrock Anionic Sulfonated Alkyl Ester (Diamond Shamrock)
Effectiveness	94% reduction 93,000 mg/kg to 5,100 mg/kg	Laboratory Columns: 75 - 94 % Reduction Field Tests: no Significant Difference in Pre and Post
Problems	None Reported	Flocculation and Pore Plugging led to Decreased Permeability
Economics	None Given	$540,000 to Remove 25,000 gal.

Field Studies

Former Wood Treating Site (Sale and Pitts, 1989)

The objectives of a 1988 pilot test of ISSSF at a former wood treating site saturated with DNAPLs were to evaluate the feasibility of using ISSSF and gather data and experience necessary for the design of a larger scale pilot test at the site. It was eventually planned to do a full scale ISSSF remediation of the site if the data from the pilot studies indicated that ISSSF was a feasible system to remediate the area. Only information of the first pilot study is presently available (Table 5).

In the pilot study, cycles of flood water and surfactant solutions were delivered via subsurface delivery lines to a 27 foot square test cell surrounded by a sheet pile wall that extended 12 feet deep to shale underlying the aquifer (Figure 6, Page 19). Subsurface recovery drain line water was monitored and pumped to a produced fluids treatment system.

Approximately 1,860 gallons of free products (PCP and creosote) were recovered. Surfactant and other reagent consumption during the flushing were considered to be low and not a significant impediment for larger scale operations. It was concluded that ISSSF could play an important role in the recovery of the contaminant at this site and ISSSF may be applicable to many sites, however, site specific evaluation and design will determine its applicability to other sites. The researchers felt that ISSSF is in the developmental stage, but has significant potential for remediation of sandy soil with oily contamination.

Volk Field Air National Guard Base (8704th Field Training Site), Wisconsin (Nash et al., 1987)

The Air Force and the EPA undertook a joint project to demonstrate the feasibility of *in situ* surfactant enhanced soil flushing and to provide information to develop a comprehensive strategy for the decontamination of fire training areas at Air Force and Department of Defense (DOD) installations. At the Volk Field site, site characterization data and high recovery results from laboratory columns studies using actual field site soil indicated the potential feasibility of using ISSSF for remediation at this site (Table 5).

Over 60 Air Force Installation Restoration Program Reports were reviewed by the joint team to determine a site that met the following ISSSF method criteria: site area less than one acre, permeable sandy soil, common organic chemical contaminants found at many other Air Force sites, and cooperative installation officials. Volk Field Air National Guard (ANG) Base Wisconsin had received waste solvents and JP-4 fuel for a fire-training area since 1955. Officials at the base indicated strong support for the research project. Exploratory site survey and sampling in 1981 confirmed that chlorinated solvents, fuels and oils had entered the shallow ground water. Soils analyses indicated penetration of the aquifer to 30 feet (9 meters) by emulsified hydrocarbons.

Three types of synthetic surfactants, two types of natural surfactants of fatty acids and ester compounds (by-products of the biological breakdown of fuels and oils beneath the fire pit) which were present in the site ground water, and combinations of the surfactants were used to flush seven test areas. The test areas were 2 feet by 2

feet or 1 foot by 1 foot plots which were all 1 foot deep and located in the fire pit area.

Over a period of 30 years, approximately 260,000 gallons of waste solvents (chloroform, TCA, TCE, benzene, toluene and ethyl benzene) and contaminated and clean JP-4 fuel had been deposited in a circular fire training pit (40 ft diameter). During fire training exercises it is estimated that 80% of the wastes were burned leaving approximately 50,000 gallons in the soil (Table 5). In shallow wells on and down gradient from the site, high concentrations (ug/l) of volatile contaminants were the following: chloroform (130), TCA (39), TCE (100), benzene (31,000), toluene (36,000), and ethyl benzene (6,800). Oil and grease (O&G) analysis of soils next to the test cells varied greatly with a range of 1,050 to 5,800 mg/kg. Heavier nonvolatile hydrocarbons were an order of magnitude lower than the O&G measurements. Soil hydrocarbon content (mg/kg) ranged from 2.4 to 400 for aliphatics, 0.42 to 75 for aromatics and 16.7 to 1003 for unresolved hydrocarbons. High organic loading reduced the local aquifer to anaerobic conditions thus solubilizing iron to a high of 24 mg/l with pHs of 5.5 to 6.0.

Soil characterization of the site indicated 95 percent sand and 5 percent by weight fines to a depth of 10 to 15 feet (3 - 4.5 meters) where weathered sandstone was encountered. Vertical permeability of the soil in the unsaturated zone was 4 X 10^{-3} to 5 X 10^{-4} cm/sec. The shallow aquifer permeability was 5 X 10^{-2} cm/sec.

A number of surfactant solutions using synthetic commercially available synthetic surfactants and natural surfactants were used on seven test cells. Synthetic surfactants were as follows:

Surfactant 1 (S1). A mixture of ethoxylated fatty acids (Witco).

Surfactant 2 (S2). An ethoxylated alkyl phenol (Diamond Shamrock).

Surfactant 3 (S3). An anionic sulfonated alkyl ester (Diamond Shamrock). Untreated ground water with surfactants and treated clarifier effluent were used as natural surfactants. Preliminary laboratory column experiments using 1.5 percent surfactant solution (50/50 mix) of an ethoxylated alkyl phenol (Diamond Shamrock) and ethoxylated fatty acid (Witco) produced a 94 percent overall hydrocarbon reduction.

The cost for Volk Field system was estimated to be "very high." The authors estimate the cost of the surfactants would be $540,000 to remove 25,000 gallons of oil and fuel from the site. The inability to economically separate the contaminants and surfactants then reuse the surfactants is the basis of the high cost estimate. Figures for equipment, labor, and other operation and maintenance costs were not given.

Field test data did not agree with the laboratory column data. Field test data indicated there were no significant differences in pre and post wash soil contaminant levels. Lab column data indicated 75 to 94 percent contaminant recovery. The field tests experienced several problems which the lab column studies did not: a decrease in percolation was observed and the 14 pore volume target for flushing was reached in only three test cells, and a 4 inch rain occurred before soil samples could be taken. Field data indicated that the ISSSF system used was not a viable remedial method for Volk Field. With repeated flushings, the soil permeability decreased due to iron precitation. The cost of the site system was high. A need existed to separate the

contaminant and surfactant from the flushing water and to reuse the surfactant to make the system economically feasible.

Laboratory Studies

Laboratory studies of soil-hydrocarbon-surfactant interactions are more numerous than actual field site studies. Lab studies delineate fundamental concepts and interactions of a multiphase system. These concepts can be transferred to remediation of contaminated subsurface environments. Experimental parameters are outlined in Table 6.

Solubilization of Polycyclic Aromatic Hydrocarbons in Micellar Nonionic Surfactant Solutions (Edwards et al., 1991)

This study was conducted to explore partitioning of hydrophobic organic compounds in soil-water-surfactant systems. The data obtained from this experiment aided in understanding the mechanisms affecting facilitated transport and the behavior of the contaminants in surfactant-enhanced remediation of hydrophobic organic contaminants. The solubilization of PAHs in nonionic surfactant solutions for determination of the mole fraction micelle-phase/aqueous-phase partition coefficients was investigated.

Batch laboratory studies using four commercial nonionic surfactants and three PAH compounds generated solubilization data for 12 distinct systems in aqueous solutions. These data were then used to measure the effectiveness of a particular

TABLE 6

LABORATORY STUDIES DATA

Study	Contaminant	Soil	Surfactant(s)	Test/Equipment
Abdul and Gibson, 1991	Aroclor 1248 (PCB)	Sandy	Witconol SN 70	Shaker Batch Soil Column HPLC
Edwards et al., 1991	Naphthalene Phenanthrene Pyrene	None - Solubility only	Brig 30 Inepal CA-720 Tergitol NP-10 Triton X-100	LSC
Abdul et al., 1990	Automatic Transmission Fluid	Sandy - 5 mm Sieve Hydraulic Cond. = 5×10^{-3} cm/sec	Ethoxylated Alcohols Ethoxylated Nonophenols Sulfates Sulfonates	Freon Extraction Turbidimeter Interfacial Tensiometer
Gannon et al., 1989	Napthalene Biphenyl P-dichlorobenzene	Finely Ground Sand and Clay	Sodium Dodecylsulfate	Soil Columns UV Mathematical Modeling
McDermont et al., 1989	Arochlor 1242	Not described	Triton X-100 Surco 223	Shaker Table Bioremediation

TABLE 6 (Continued)

Study	Contaminant	Soil	Surfactant(s)	Test/Equipment
McDermont et al., 1989	Arochlor 1242	Not described	Triton X-100 Surco 223	Shaker Table Bioremediation
Vigon and Rubin, 1989	Anthracene Biphenyl	Artificial - 84% Ottawa Sand 12% Mineral Clay/silt 4% Soil Organics	Ethoxylates Alklyphenol Dodecylphenol Nonylphenol Dodecyl	GC - Anthracene LSC - Biphenyl
Rajput, 1988	Phenol, TCE Chlorophenol Octane, Toluene Chlorobenzene Aniline	Purchased Sand and Sandy Loam	Witconol NS- 500K	Shaker Table GC
Ellis et al., 1985	Murban Crude Oil PCBs Chlorophenols	Fine to Coarse Loam Hydraulic Cond. = 10^{-2} to 10^{-4} cm/sec	Adsee 799 NP 90 - Combined Nonionics	Shaker Table Soil Columns

surfactant in solubilizing a given solubilate by predicting PAH compound partitioning between water, surfactant micelles and soil.

Four commercially available polyoxyethylene (POE) nonionic surfactants were used: Brij 30, Igepal CA-720, Tergitol NP-10, and Triton X-100. These surfactants represent more than 70% of the nonionic surfactants produced in the U.S. in 1986. Prior experimentation of the solubilization of PAH compounds in soil/water suspensions formed the basis for surfactant selection (Liu et al., 1991).

The data were used to calculate the molar solubilization ratio and the PAH mole fraction micelle-phase/aqueous-phase partition coefficient, K_m. Above the CMC, PAH solubility increased linearly with surfactant dose. The PAH compounds were solubilized in the range of 0.04 to 0.4 mol of PAH/mol of micellar surfactant. K_m values ranged from $10^{4.6}$ to $10^{6.5}$. For a particular surfactant-PAH system, the log K_m correlated with the PAH octanol-water partition coefficient.

Selection of Surfactants for the Removal of Petroleum Products from Shallow Sandy Aquifers (Abdul et al., 1990)

The suitability of 10 commercial surfactants for washing residual levels of automatic transmission fluid (ATF) from sandy soil was evaluated in this 1990 laboratory study. For the evaluation, several properties of aqueous surfactant solutions were measured: CMC, soil dispersion, surfactant solubilization of the contaminant, soil washing effectiveness.

Batch samples consisted of 5 g soil contaminated with 0.2385 g ATF and 100 ml of 0.5% (V/V) aqueous surfactant in a beaker. The sandy soil from an aquifer

was air dried and passed through a 0.5 mm sieve. The average hydraulic conductivity of the sand was 5 x 10^{-3} cm/sec.

Surfactant selection was based on the following properties: solubility in oil and water, detergency, oil dispersion, emulsification, foaming, wetting, and other physical-chemical and biological properties. The 10 surfactants selected for the study represent the four main groups of commercial surfactants: ethoxylated alcohols (nonionic), ethoxylated nonylphenols (nonionic), sulfates (anionic), and sulfonates (anionic).

The selected surfactants differed in their ability to remove the ATF from the soil with a range of 33.1 to 83.8 percent mass recovered. Surfactants that cause high soil dispersion are less suitable for soil washing than surfactants with low soil dispersion. From the data analysis and correlation of the various tests, the investigators concluded that surfactants with low CMC, good detergency and solubilization potential, low soil dispersion, and were biodegradable were the best candidates for soil washing of ATF.

Treatment of Contaminated Soils with Aqueous Surfactants (Ellis et al., 1985)

In one of the first major projects to transfer EOR technology to *in situ* remediation of hazardous waste sites, a literature search determined the nature and quantities of contaminants at Superfund sites and the applicability of existing technology to *in situ* treatment of contaminated soils. Follow-up laboratory batch and column studies were conducted to improve methodology applicable to ISSSF of soils contaminated with organic chemicals.

The literature review determined three contaminate groups: (1) slightly water soluble organics (aromatic and halogenated hydrocarbon solvents and chlorophenols), (2) heavy metal compounds, and (3) hydrophobic organics (PCBs and aliphatic hydrocarbons). For the lab studies, Murban crude oil, a PCB mixture in chlorobenzenes, and a mixture of di, tri- and pentachlorophenols were used.

ISSSF was determined to be the most feasible and practical remediation method under the following conditions:

* a large volume of subsurface contaminated soil involved (100 to 100,000 m^3 with 1 to 10 m depth)
* contaminant concentration of < 10,000 ppm or higher concentrations at site removed or sealed off
* the contaminants can be dissolved or suspended in the flushing solution, degraded to nontoxic products, or rendered immobile

Other remediation methods were thought to be more practical for deeper or more highly contaminated areas.

Shaker table studies involved a series of 3 water washes, 3 surfactant solution washes, and 3 final water washes for 30 -100 gm of contaminated soil. Soil columns (3 in x 5 ft - 7.6 cm x 152 cm) were washed with water and the surfactant solution by gravity feed with a constant 61 cm (2 ft) head. The surfactant selection decision was based on the following surfactant features: high water solubility, good dispersion of Murban hydrocarbons, minimal fine soil particle suspension, adequate biodegradability, and minimal analytical interferences.

Water washes alone removed the chlorophenols but were not effective in removing the oil or PCBs. The surfactant solution removed 93% of the oil and 98% of the PCBs from the soil in both the shaker and column studies.

The authors concluded that surfactant solutions have the potential to be used in *in situ* remediation of hydrophobic organic compounds in soil at sites with similar soil characteristics. Further development of the ISSSF system on a larger scale was warranted. The authors believe that cost effective application of the technique would involve reuse of the surfactant Surfactant combinations may be more effective than single surfactant solutions.

Practical Consideration in the Surfactant-aided Mobilization of Contaminants in Aquifers (Vigon and Rubin, 1989)

In an effort to predict surfactant effectiveness for aquifer restoration, surfactant selection and dosage optimization parameters were systematically evaluated. Factors relevant to the interactions between surfactant solutions, aquifer material, and hazardous organic chemicals that were systematically investigated included surface tension minimization, CMC, hydrophile-lipophile balance number (HLB), solubilization efficiency and partition coefficient. Test procedures for measuring some surfactant performance parameters were developed in the laboratory. Anthracene and biphenyl were the model organic compounds used in the study. EPA defined synthetic ground water and artificial soil (84% Ottawa sand, 12% mineral clay/silt, and 4% soil organic matter) were used.

Results of previous studies using surfactants in EOR and ISSSF demonstrated the feasibility of surfactant-aided aquifer restoration (Hill et al., 1973; Doscher, 1977;

Shah, 1981; Ellis et al., 1985). The researchers felt there was a need for established criteria for the rational selection of surfactant type and dose instead of the trial and error method used previously.

Surfactant selection criteria included favorable solubility at ground water temperatures, relative lack of toxicity, and range of structures. Solutions of 0.1 to 1% (by weight) active ingredients were used.

The addition of the surfactant solution increased the aqueous phase concentration of both contaminants, i.e., the partition coefficients were reduced. At surfactant solutions of 1%, up to 90% contaminant removal was achieved. With ground water alone, 2 to 3% contaminant removal was achieved. At doses above 0.1% weight, all surfactants reduced the partition coefficients of the contaminants. The surfactant solutions studied affected ground water properties to a very limited extent.

Laboratory Studies of Surfactant-Enhanced Washing of Polychlorinated Biphenyl from Sandy Material (Abdul and Gibson, 1991)

Laboratory batch and column studies were used to assess the suitability of an alcohol ethoxylate surfactant (Witconol SN70) for washing three concentrations of Aroclor 1248 from sandy soil. Various concentrations of surfactant solution and PCBs were used. Adsorption breakthrough curves were plotted. The results of the surfactant washings and water alone washings were compared.

Favorable results from a previous laboratory study were cited as the basis of this study (Abdul et al., 1990). This study evaluated the effectiveness of a surfactant, selected from the previous study, to enhance the washing of a PCB from sandy soil.

The previous study indicated alcohol ethoxylate surfactants were more effective in washing petroleum hydrocarbons from soil than the other three groups of surfactants tested (Abdul et al., 1990). Ethoxylate surfactants were shown to cause minimum dispersion of soil colloids, had low critical micelle concentrations, caused high solubilization and dispersion of the low water solubility oil, and washed 80% of the oil from sandy soil in batch studies.

The plotted equilibrium isotherm for the adsorption of the surfactant to the soil was a S-shaped (Langmuir) curve approximately symmetrical about the 0.5% surfactant concentration. The 1% surfactant solution was the most effective in washing the PCB from the soil column. After 20 pore volumes of washing, the 1% surfactant solution reduced the PCB in the sand from 1728 to 251 mg/kg (86%).

The washing success of the alcohol ethoxylate surfactant used in this study maked it a good candidate for *in situ* soil flushing of PCBs. Even at low clay and TOC soil content, surfactants will adsorb to the soil. Therefore, optimum surfactant concentration should be determined in lab studies resembling the site specific field conditions before field studies are done. ISSSF is a site specific method and its success depends on the physical, chemical and hydrologic properties of the components involved.

Treatment of Hazardous Waste Contaminated Soils by Extraction and Washing (Rajput, 1988)

The effectiveness of using surfactants as an extraction and washing agent for contaminated soil was explored in the laboratory study. A series of experiments were performed in three phases using several surfactants, seven hydrocarbons which were

representative of major industrial wastes, and two soils (sand and sandy loam). Phase one used shaker table experiments to determine the solubilization and extractive efficiencies of 1) several different surfactants and 2) one particular surfactant selected previously. Phase two used gravity flow contaminated soil columns to study the extraction and washing efficiency of surfactant solutions with stationary soil. Phase three used bench scale batch experiments to study the removal of the contaminants from the soil using mechanical mixers.

The organic compounds used to represent the major industrial wastes were the following: phenol, 2,4-dichlorophenol, octane, trichloroethylene (TCE), toluene, 1,2,4-trichlorobenzene, and aniline. Although the study was intended for application to excavated soil, the resulting data and conclusions apply to *in situ* remediation as well. The investigator chose soil washing as an alternative over to other remedial systems to alleviate the problem of disposal at approved hazardous waste sites. Also, an on site system was advantageous as opposed to hauling the contaminated soil off site.

The selected surfactants had to meet the following criteria:

* soluble in deionized water at the desired concentration
* commercially available
* able to solubilize the organics form the soil in a reasonably short time
* exhibit desirable dispersion and settling behaviors

All the surfactants tested were from the Witco Chemical Corporation. Results of the column studies determined that a 2% aqueous solution of Witconol NS-500K solution was appropriate in the bench scale batch study.

In the phase one shaker table study, cationic surfactants were determined to be unsuitable for contaminant removal. The phenols and aniline had the highest solubilities (6.7 to 0.46 g/100 ml water). Those contaminants had the highest recovery rates by the surfactants (92.5 - 98.1%) and water (88.4 - 93.9%). The recovery rates of the less soluble compounds, octane (0.002 g/100 ml), 1,2,4-Trichlorobenzene (0.005 g/100 ml), toluene (0.047 g/100 ml) and TCE (insoluble), were lower. Surfactant washes recovered 27.8 to 33.0% of the contaminants and water washes recovered 15.0 to 27.7%.

In the phase two column studies, Witconol NS-500K gave the best removal efficiency of 1,2,4-trichlorobenzene from the soil. A 2% surfactant solution gave better efficiency (98.6%) than the 1% solution (75.2%) and the water wash (33.0%).

In the phase three bench scale study, the water washes removed more than 91% of the aniline, phenol, and dichlorophenol and 65% of the 1,2,4-trichlorobenzene from the soil. The 2% aqueous solution of Witconol NS-500K removed 92.9% of the 1,2,4-trichlorobenzene, 91.5% of the aniline, 96.6% of the phenol, and 95.3% of the 2,4-dichlorophenol from the soil.

A number of conclusions were drawn from this study. The test contaminants were washed/extracted from the test soils. The test contaminants, phenol, 2,4-dichlorophenol, and aniline, are relatively water soluble and were effectively removed from the soil by water alone. Surfactants varied in their efficiency in washing/extracting the hydrophobic contaminant, 1,2,4-trichlorobenzene, from soil. A cationic surfactant was found unsuitable as an extracting agent; nonionic surfactants were more efficient. With the most effective surfactant, a 2% solution was found to

be more effective than a 1% solution. The washed soil contained residual concentrations of the contaminants.

Surfactant Scrubbing of Hazardous Chemicals from Soil (Clement and Rickabaugh, 1986)

Soil from a hazardous waste site contaminated with pesticides and other chlorinated hydrocarbons, solvents, waste oils and other wastes was used in this lab study. The effectiveness of fourteen aqueous surfactants and surfactant blends to decontaminate the soil was determined by lab scale batch and flow-through column experiments. Also, the use of photolysis to decontaminate the surfactant solutions was investigated. Gas chromatography (GC) was used for hydrocarbon analysis.

The soil collected at the site contained a total of 2078 mg/kg chlorinated hydrocarbons in the 52 peaks determined by GC. Eleven specific compounds were found (216 - 266 mg/kg) and tracked in the experiments: hexachlorobenzene, several di- and trichlorobenzenes, hexachlorobutadiene, Aldrin, Endrin, Heptachlor, and Dieldrin.

Technology transfer of the use of surfactants in EOR influenced the investigators to apply the technology to soil remediation. Favorable results from previous investigations (Huibreste et al., 1980, Botre et al., 1978, and Ellis et al., 1985) were cited which also indicated the feasibility of surfactant flushing of contaminated soils.

Of the 38 commercial anionic, nonionic and cationic surfactants collected for the study, 14 were selected. Criteria for the selection were as follows: good water solubility, near neutral pH for minimal soil adsorption, generally low chloride content

(except for the cationic). Surfactants for the column studies were selected from the results of the batch tests.

In the total organic halogen batch studies (TOX), there was little difference in the anionic and nonionic surfactant removal efficiencies. On the average, the 2% solutions removed more of the TOX (90 mg/kg) than the 1% (62 mg/kg) or the 0.5% (30 mg/kg). The highest nonionic TOX removal was 150 mg/kg.

In the batch studies, the 2% anionic solutions performed best removing 47.1 mg/kg (20.8%) of the 11 tracked hydrocarbons. Most surfactants performed well in removing hexachlorobenzene, Endrin, Aldrin, and hexachlorobutadiene. Cationic surfactants were better at removing the lower molecular weight compounds than the other surfactants.

In the column studies, water alone removed less than 1% of the tracked contaminants while removals of 59% were obtained with the surfactants. The 2% surfactant blends were more successful than the other surfactant types: 18.7 mg/kg removal indicated in the leachate and 115 mg/kg removal indicated in the soil extract. In the liquid-liquid extraction procedure, emulsion problems caused erratic extraction efficiencies. Soil extractions indicated more of the contaminant had been removed than the liquid extractions indicated. The 3 week column study indicated that the removal rates of specific compounds decreased with time.

It was postulated that the greater contaminant removal shown by the column studies was due to two experimental conditions. The batch data used liquid-liquid extraction which had emulsion problems and the column data reflected a one week flushing or contact time as opposed to one day with the batch studies.

In the photolysis experiments of the column leachate, 76 to 100% of the 11 tracked chlorinated hydrocarbons were destroyed by the lamps in 24 hours. Photolysis shows promise as a remediation technique for chlorinated hydrocarbon contaminants.

A number of conclusions were drawn from the study. Surfactant solutions enhanced the removal of chlorinated hydrocarbons from the soil. The most effective surfactant solution concentration was 2%. Blends of surfactant types generally gave better removal efficiencies than a single surfactant. Liquid-liquid extractions had emulsion problems which inhibited the efficiency of the gas chromatography detection method. Photolysis showed promise as a decontamination technique for the surfactant leachate obtained in this study.

Two Strategies for Soil Remediation: Biodegradation and Surfactant Extraction (McDermott et al., 1989)

The objective of this study was to develop two strategies for remediating PCB-contaminated soil: biodegradation by bacteria and extraction by aqueous surfactant solutions. Three laboratory biodegradation experiments were performed using three bacteria strains and actual site and laboratory soils contaminated with PCB. The first study used incubated shaker batches, the second study simulated field conditions (less water, cooler temperatures, less aeration, and no agitation), in the third study the sample was dosed three times weekly, for 23 weeks, and stirred after each application. *In situ* field tests of two 3m x 3m plots were carried out for 13 weeks.

The surfactant extraction technique involved extraction of the PCB from soil and concentration in a precipitate that is 2 - 3% of the original soil mass. Bench-

scale studies used crushed excavated PCB contaminated soil in a multi-stage counter-current extraction/washing procedure where the PCB is transferred to the aqueous phase. Three solid/liquid separation processes were explored: use of thickeners, filters and centrifugation. Designs for effluent treatment systems for surfactant removal and further waste water treatment were outlined.

Aroclor 1242 contaminated soil (525 ppm) from a former drag racing site was used. In addition, laboratory contaminated soils with spikes of 50 and 500 ppm Aroclor 1242 and 50 ppm Aroclor 1254 were used.

Permanent destruction of the PCB contaminated soil was favored by the investigators. Landfilling excavated PCB contaminated soil was not viewed as a feasible remediation technique.

Biodegradability was a prime concern in surfactant selection. Good capability for solubilizing PCB and ease of separation of PCB and the surfactant from the process stream were other desirable surfactant characteristics. Triton X-100 (Rohm and Hass) and Surco 233 (Onyx Chemical Company) were used in 1 to 3% concentrations. These surfactants were shown to increase the solubility of Aroclor 1260 in water from 2 to 3 ppb to several thousand ppm. The percent adsorption onto the soil varied markedly for each surfactant: 15 to 20% for the Triton X-100 and less than 1% for the Surco 233. The adsorption characteristic led to different performances for each surfactant.

In the shaker batch study, rapid degradation of the PCB occurred. The reported results were as follows:

* 95% in one day by MB1 and LB400 of the 50 ppm Aroclor 1242
* 85% in two days by LB400 of the 500 ppm Aroclor 1242
* 65% in one day by LB400 of the 50 ppm Aroclor 1254

In the laboratory field simulation study, the cell count at depths lower than 1 cm was approximately one tenth of the count in the top 1 cm. First signs of degradation in the unstirred sample occurred in the top 1 cm of soil in 30 days. After 15 weeks, 50% of the PCB had been degraded in the top 1 cm of soil and 10% in the lower depths. In the sample stirred after 3 months, the greatest degradation again occurred in the top centimeter.

In the study that mixed the sample after each thrice weekly cell dosage, after 23 weeks, 35% of the PCB had been degraded at all depths to 15 cm. The total of PCB degraded in this study was more than in the unstirred sample. In one control experiment, the thrice weekly dosing with heat-killed LB400 bacteria resulted in the proliferation of indigenous bacteria that degraded a small amount of PCB.

The biodegradation rate of the field test was about 50% of rate of the lab experiments. The first detection of degradation was at 8 to 10 weeks (20% of the PCB in the top 3 cm of soil). At 18 weeks, the top 3 cm of soil showed 25% PCB degradation in the unmixed soil and 10% in the mixed half. At week 18, cool weather greatly reduced activity. In the control plot, there was no evidence of any PCB degradation.

In the surfactant washing preliminary studies, the clay constituents of the soil made the use of thickeners and/or filters not feasible as unit operation for the solid/liquid separation process. Centrifugation was the only viable option for solid/liquid separation. The preliminary studies indicated that 1% Surco 233 to be the better surfactant for further studies since less than 1% of it was adsorbed onto the clay as opposed to 15 to 20% adsorption of the Triton X-100. The similar soils selected for further study (Oakland surface and drag strip site) were heavy clayey soils, mostly montmorillonite. Investigation of several methods to separate PCB from the process effluent indicated chemical precipitation with a divalent cation to be most effective.

In the final bench-scale process, the initial 1,000 ppm PCB spiked soil concentration was reduced to 40 ppm. The actual site soil PCB concentration of 100 to 168 ppm Aroclor 1260 was reduced to 18 to 24 ppm. The precipitate from the unit contained around 2.6% PCBs and the effluent contained 1.8 ppb PCB. It appeared that the differences in site soil from the spiked soil, contaminant level, age of contamination, and mode of contamination, may have influenced the results.

The investigators concluded that both strategies showed promise for safe economical remediation of PCB contaminated soils, but require further study. The loss of the surfactant in the precipitate and the incineration of the precipitate are felt to be the major costs of the surfactant washing process.

Soil Clean Up by *In Situ* Surfactant Flushing. III. Laboratory Results (Gannon et al., 1989)

This laboratory study investigated the feasibility of using sodium dodecylsulfate (SDS), an anionic surfactant, for ISSSF. The study was conducted in three parts: solubilization of the model compounds in a magnetic stirrer, column flushing of contaminated ground clay soil, and hexane extraction of p-dichlorobenzene (DCB) in the flushing solution to recover the surfactant solution for reuse. A model for the prediction of the solubilization behavior of surfactants was developed and experimentally tested.

Naphthalene, biphenyl and p-dichlorobenzene (DCB) were the model compounds used in the study. The preceding compounds were expected to emulate the contaminants benzene, toluene, PCBs, and chlorinated solvents.

The favorable results obtained by Ellis et al. (1985) encouraged the investigators to pursue further studies recommended by the Ellis et al. study. *In situ* vapor extraction was considered an efficient cost-effective method, but not for the hydrophobic DNAPLs used in the study.

Sodium dodecylsulfate (SDS) was selected for the following characteristics: inexpensive, nontoxic, and anionic. An anionic surfactant having a low solubility was desired to allow recovery of the surfactant by solvent extraction for the recycling or reuse of the surfactant.

In the solubility study, effective solubility (true solubility plus solubilization in micelles) of the model hydrophobic compounds increased by factors of 20 to 100 in the surfactant solution.

Only a fraction of the spiked contaminant was recovered in the surfactant elutriate in the column flushing study. Further investigation indicated approximately two-thirds of the spike was lost during the hexane evaporation. Clay:sand ratios larger than 1:3 had flow rates too slow for convenient measurement. Although the flow rates were slower through the samples with the larger proportion of clay, the contaminant removal efficiency was greater. In the rapid flow rate samples 65% of DCB was removed and in the slow flow rate samples, more than 90% was removed.

In the surfactant recovery studies, 90 to 95% removal of the contaminant in 24 hours was achieved with the gentle mixing extraction. The recovered surfactant solution was as effective as fresh solution in solubilizing biphenyl. In the countercurrent extraction study, 95% removal of the contaminant from the aqueous surfactant solution was achieved in 3 to 9.5 hours.

The model was tested with solubilization data from the first study. C_{TOTAL} values (moles solute in aqueous phase + moles solute in micelle interiors/total volume of solution) versus C_{SURF} values (total molar surfactant concentration) were plotted. The theoretical slopes from the model calculations and actual experimental slopes were compared. The slopes predicted from the theoretical solubilization model and the actual observed slope of C_{TOTAL} versus C_{SURF} were quite close. The model produce a very good estimate of the solubilizing power of the surfactant for the hydrophobic contaminants.

Several conclusions were drawn from the studies. The micelles of ionic surfactants greatly increased the solubilities of the model hydrophobic compounds. SDS mobilized hydrophobic organics sorbed on soils. The greater the equilibrium or

contact time between the soil and aqueous phases, the greater the removal efficiency. A gentle nonpolar solvent extraction system is an effective method for recovering the surfactant solution for reuse. A simple model can be used to estimate the solubilizing power of a surfactant for any particular hydrophobic contaminant.

CHAPTER III

MATERIALS AND METHODS

Introduction

This experimental laboratory study was designed to determine if selected surfactants in aqueous solutions with varying pH and brine conditions could enhance the desorption of hydrophobic hydrocarbons from sandy soil. The study tested the influence of the selected variables (Table 7) in batch shaker experiments. The site-specific variables include target compound, target compound concentration, and the possible levels of brine and pH in the ground water and/or soil. Variables which could be altered on site include surfactant and surfactant concentration. The hypotheses stated in the introduction were tested by statistics which determined if the differences in the flushing solutions were significant. This study was derived from recommendations of reports addressing multi-phased contaminants in soil (Ellis et al., 1985; Comstock and Stirling, 1986)

The selected surfactants (Ss) were Sandoxylate SX-408 (Sandoz Chemicals Corporation), InProve (Unique Products, Inc.) and NAXCHEM DISPERSANT K (Ruetgers-Nease Chemical Co., Inc.). The surfactant concentration (SC) range used (0.5 - 2.0 %) was recommended by the manufacturers and commonly used

TABLE 7

EXPERIMENTAL VARIABLES

Variable	Symbol	Name or Value
Surfactant #1	S1	Sandoxylate SX-408
Surfactant #2	S2	NAXCHEM DISPERSANT K™
Surfactant #3	S3	InProve
Surfactant Concentration #1	SC1	0.5%
Surfactant Concentration #2	SC2	1.0%
Surfactant Concentration #3	SC3	2.0%
Target Compound #1	TC1	Hexadecane
Target Compound #2	TC2	O-Cresol
Target Compound #3	TC3	Phenanthrene
Target Compound Concentration #1	TCC1	4.620 mg/g soil
Target Compound Concentration #2	TCC2	9.240 mg/g soil
Target Compound Concentration #3	TCC3	13.860 mg/g soil
pH #1	pH1	5.5
pH #2	pH2	7.0
pH #3	pH3	8.5
Brine #1	B1	1,000 mg/l
Brine #2	B2	5,000 mg/l
Brine #3	B3	10,000 mg/l

concentrations in other research projects (Abdul and Gibson, 1991; Clement and Rickabaugh, 1986; Ellis et al., 1985; Vigon and Rubin, 1989).

The three experimental target compounds (TCs) were hexadecane, o-cresol and phenanthrene. The target compound loading range (4.62 - 13.86 mg TC/kg soil) represents concentrations reported at waste sites (Ellis et al., 1985). Unlabeled target conpounds mixed with ^{14}C labeled target compounds and a liquid scintillation counter (LSC) were used to quantify and track the adsorption/desorption of the compounds.

Brine (B) and pH were the ground water quality parameters selected as experimental variables due to their wide spread variability. The pH of the soil has been shown to influence the loss rates of organic chemicals from contaminated soil (Loehr and Matthews, 1992). The selected pH range of 5.5 to 8.5 represents the most common ground water conditions (Nash et al., 1987). The brine concentrations (1,000, 5,000 and 10,000 mg/l) represent concentrations in fresh, brackish and saline water, respectively, (Freeze and Cherry, 1979; Driscoll, 1986). Inert dissolved salts have been known to decrease the effectiveness of some types of surfactants (Gannon et al., 1989). High dissolved salt concentration have been demonstrated to drastically reduce the effectiveness of *in situ* surfactant-enhanced soil flushing system at a Texas site (Fountain, 1992).

Experimental Design and Procedures

Experimental Design

Each combination of all possible sample variables was assigned a sample number. For each sample block of one target compound and one surfactant, there were 81 sample numbers (Table 8). A total of nine sample data blocks, or nine combinations of target compounds and surfactants, comprised entire data matrix (Table 9). For each target compound, therefore, there were a total of 243 sample numbers with the three different surfactants (Table 10). With the three target compounds, each with three different surfactants, there were a total of 769 sample numbers. Each sample number had three replicates, one water flush and one blank for a total of 3845 samples prepared.

Sample Preparation

The experimental sample preparation steps are outlined in Table 11. The ^{14}C and the unlabeled reagents were diluted with spectra-grade solvents to the desired concentrations. Batch reactors consisted of ^{14}C labeled contaminated soil (or unlabeled blanks) and surfactant solution in 7 ml glass scintillation vials (Kimble). The vials were shaken until a previously determined equilibrium was attained, then centrifuged in an IEC Centra-7 centrifuge. An aliquot of the supernatant from each reactor vial was then transferred to a 7 ml glass scintillation vial containing Ecolume scintillation cocktail (ICN Biomedicals, Inc.). The ^{14}C reading vials were placed in a

TABLE 8

EXAMPLE DATA BLOCK FOR EACH TARGET COMPOUND - SURFACTANT COMBINATION

			HEXADECANE								
			TCC1 (4.620 MG/G)			TCC2 9.240 MG/G)			TCC3 13.860 MG/G)		
			BRINE*			BRINE			BRINE		
			B1 1*	B2 5	B3 10	B1 1	B2 5	B3 10	B1 1	B2 5	B3 10
		pH									
SANDOXYLATE SX 408	SC1 0.5 %	5.5	1#	4	7	28	31	34	55	58	61
		7.0	2	5	8	29	32	35	56	59	62
		8.5	3	6	9	30	33	36	57	60	63
	SC2 1.0 %	5.5	10	13	16	37	40	43	64	67	70
		7.0	11	14	17	38	41	44	65	68	71
		8.5	12	15	18	39	42	45	66	69	72
	SC3 2.0 %	5.5	19	22	25	46	49	52	73	76	79
		7.0	20	23	26	47	50	53	74	77	80
		8.5	21	24	27	48	51	54	75	78	81

* BRINE Concentrations = Thousands mg/l
\# Each Sample = 3 Replicates (Averaged)
1 Water Flush
1 Blank

TABLE 9

DATA MATRIX COMPOSED OF BLOCKS FROM TABLE 8

		TC1	TC2	TC3
		HEXADECANE	O-CRESOL	PHENANTHRENE
S1	SX 408	BLOCK 1 TC1S1	BLOCK 2 TC2S1	BLOCK 3 TC3S1
S2	NAXCHEMK	BLOCK 4 TC1S2	BLOCK 5 TC2S2	BLOCK 6 TC3S2
S3	INPROVE	BLOCK 7 TC1S3	BLOCK 8 TC2S3	BLOCK 9 TC3S3

TABLE 10

SAMPLE NUMBERING SCHEME, ONE TABLE FOR EACH TARGET COMPOUND

			TC CONC. # 1			TC CONC. # 2			TC CONC. # 3		
		pH	B1	B2	B3	B1	B2	B3	B1	B2	B3
SURFACTANT #1	CONC 1	5.5	1	4	7	28	31	34	55	58	61
		7.0	2	5	8	29	32	35	56	59	62
		8.5	3	6	9	30	33	36	57	60	63
	CONC 2	5.5	10	13	16	37	40	43	64	67	70
		7.0	11	14	17	38	41	44	65	68	71
		8.5	12	15	18	39	42	45	66	69	72
	CONC 3	5.5	19	22	25	46	49	52	73	76	79
		7.0	20	23	26	47	50	53	74	77	80
		8.5	21	24	27	48	51	54	75	78	81
SURFACTANT #2	CONC 1	5.5	82	85	88	109	112	115	136	139	142
		7.0	83	86	89	110	113	116	137	140	143
		8.5	84	87	90	111	114	117	138	141	144
	CONC 2	5.5	91	94	97	118	121	124	145	148	151
		7.0	92	95	98	119	122	125	146	149	152
		8.5	93	96	99	120	123	126	147	150	153
	CONC 3	5.5	100	103	106	127	130	133	154	157	160
		7.0	101	104	107	128	131	134	155	158	161
		8.5	102	105	108	129	132	135	156	159	162
SURFACTANT #3	CONC 1	5.5	163	166	169	19	193	196	217	220	223
		7.0	164	167	170	191	194	197	218	221	224
		8.5	165	168	171	192	195	198	219	222	225
	CONC 2	5.5	172	175	178	199	202	205	226	229	232
		7.0	173	176	179	200	203	206	227	230	233
		8.5	174	177	180	201	204	207	228	231	234
	CONC 3	5.5	181	184	187	208	211	214	235	238	241
		7.0	182	185	188	209	212	215	236	239	242
		8.5	183	186	189	210	213	216	237	240	243

TABLE 11

SAMPLE PREPARATION STEPS

Step	Task
1	Weigh out 0.5 g of soil into 7 ml glass vials
2	Put vials into boxes with identifying labels
3	Contaminate soil in vials with 0.5 ml of ^{14}C target compounds in solvent or blank solution
4	Evaporate solvent from contaminated soil in hood
5	Prepare surfactant-brine solutions and adjust pH
6	Add 5.0 ml surfactant solution or water to contaminated soil
7	Shake vials 6 hours on reciprocating shaker (low - 180 oscillations/min)
8	Centrifuge vials 30 minutes at 2500 rpm
9	Add 5.0 ml Ecolume scintillation cocktail
10	Label and number lids to counting vials
11	Pipette 1.0 ml from shaker vial to corresponding counting vial
12	Calibrate scintillation counter
13	Put vials into liquid scintillation counter in sequence and read for 20 minutes each

Beckman LS 7000 Scintillation Counter (LSC) for determination of the radioactivity of the flushed surfactant solution.

Three sample types were tested, true samples, ^{14}C blanks, and water washes (Table 12). True samples consisted of ^{14}C contaminated soil and surfactant solution. The ^{14}C blanks checked for background radioactivity. The blanks were the same as the true samples except that the contaminated soil had no radiolabeled target compound on it. The water washes were the same as the samples except there was no surfactant in the flushing solution. Triplicates of the true samples were prepared.

Quality control procedures in sample preparation included blanks to account for background radiation, triplicates of the true sample, shaker equilibrium studies, quench curves, evaporation loss studies and use of the same batches of prepared solutions for the entire batch of target compound samples. The samples were read by the LSC for 20 minutes or for 2 standard deviation readings, which ever came first.

Shaker Equilibrium Studies

To equilibrate the dynamics of the soil-target compound-surfactant solution system in the batch reactors, the vials were shaken on a Eberbach Corporation model 6010 oscillating shaker at 180 oscillations per minute. Experiments were performed to determine the time for the surfactant solution, soil and target compound to reach equilibrium in the batch reactors. These experiments were performed for each combination of the following variables: target compounds, target compound concentrations, surfactants and surfactant concentrations. Reactor vials were removed from the shaker at timed intervals and the concentration of the target compound in the

TABLE 12

SAMPLE TYPE AND VARIABLE AMOUNT

Sample Type	Batch Reactor Vials				Reading Vials	
	Soil (g)	Surfactant Solution (ml)	^{14}C & Cold Target Compound (ml)	Cold Target Compound (ml)	Batch Reactor Solution (ml)	Cocktail (ml)
True Sample	0.5	5.0	0.5	0.0	1.0	5.0
TC Blank	0.5	5.0	0.0	0.5	1.0	5.0
Water Wash	0.5	0.0	0.5	0.0	1.0	5.0

solution determined by the LSC. The equilibrium time was determined to be the time beyond which there was no change in the LSC readings of the sample solution (Figure 7). Initially, the target compound appeared to remain on the contaminated soil. With continued shaking, however, the target compound appeared to desorb from the soil, increased in the liquid phase and reached equlibrium with the surfactant solution.

Quench Curves

Interference in ^{14}C counting efficiency of a LSC is called quenching. Interferences result in reduced detection efficiency from photon energy loss (Kobayashi et al., 1988). The energy losses in the transfer of the ^{14}C photons from the sample to the detector can be caused from chemical quenching (photon loss from solvent to solute) and/or color quenching (attenuation of light photons in the solution)(Kolb, 1988). When the number of ^{14}C photons in the sample is reduced and not read by the LSC, quenching occurs.

Performing quench curve corrections accounts for the photon losses and reduced system efficiency. The resulting data, in ^{14}C counts per minute (CPM), are used for corrected concentration determinations. LSC data from samples with the same amount of ^{14}C labeled compound and varying amounts of sample solution (TC + surfactant solution + brine) are plotted against the concentration of the solution to form the quench curve (Figure 8). These data are compared to curves from standardized quench samples (Figure 9). If quenching occurs in samples, readings are corrected for the interference. Quench curve analyses were performed for every

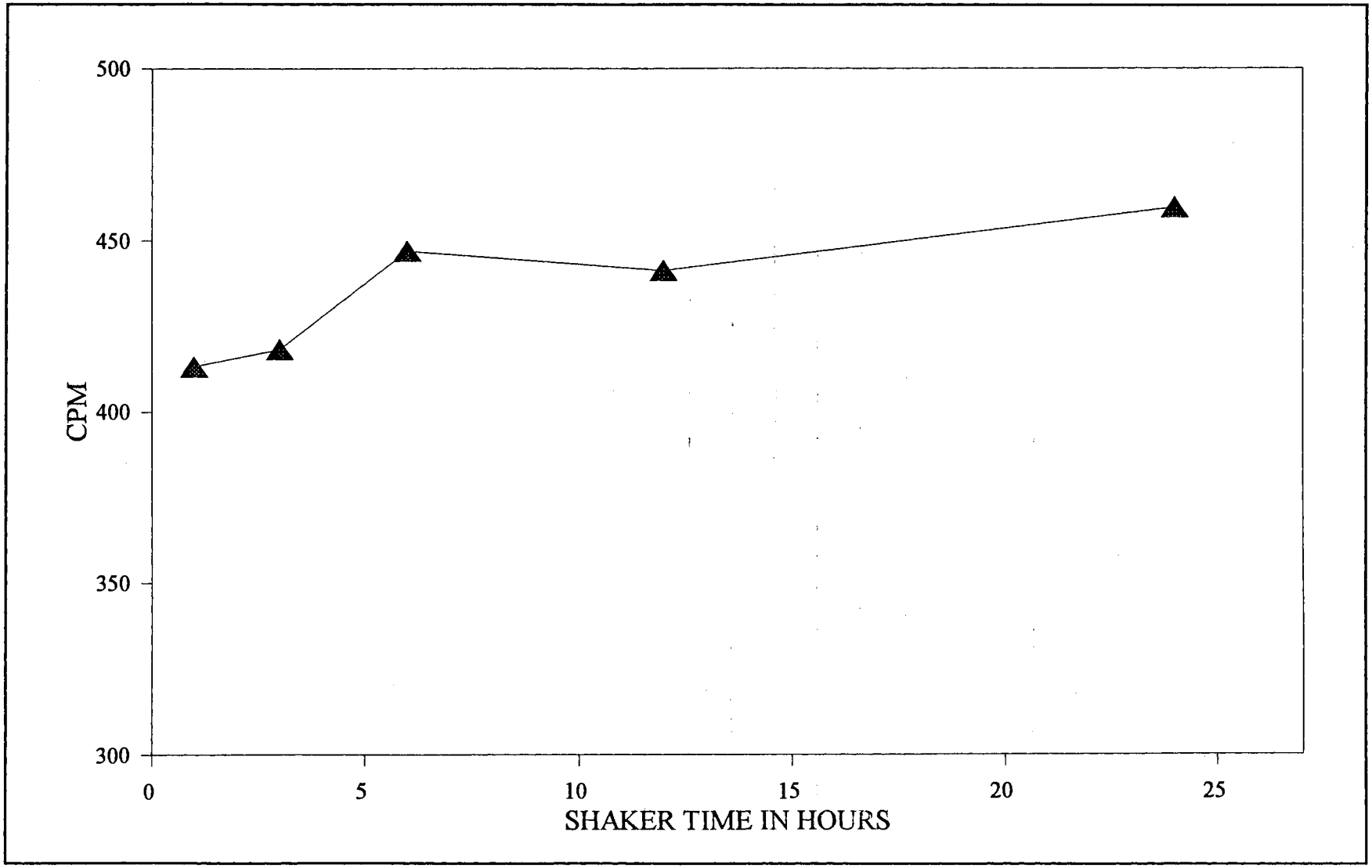

Figure 7. Example of Shaker Equilibrium-Time Curve

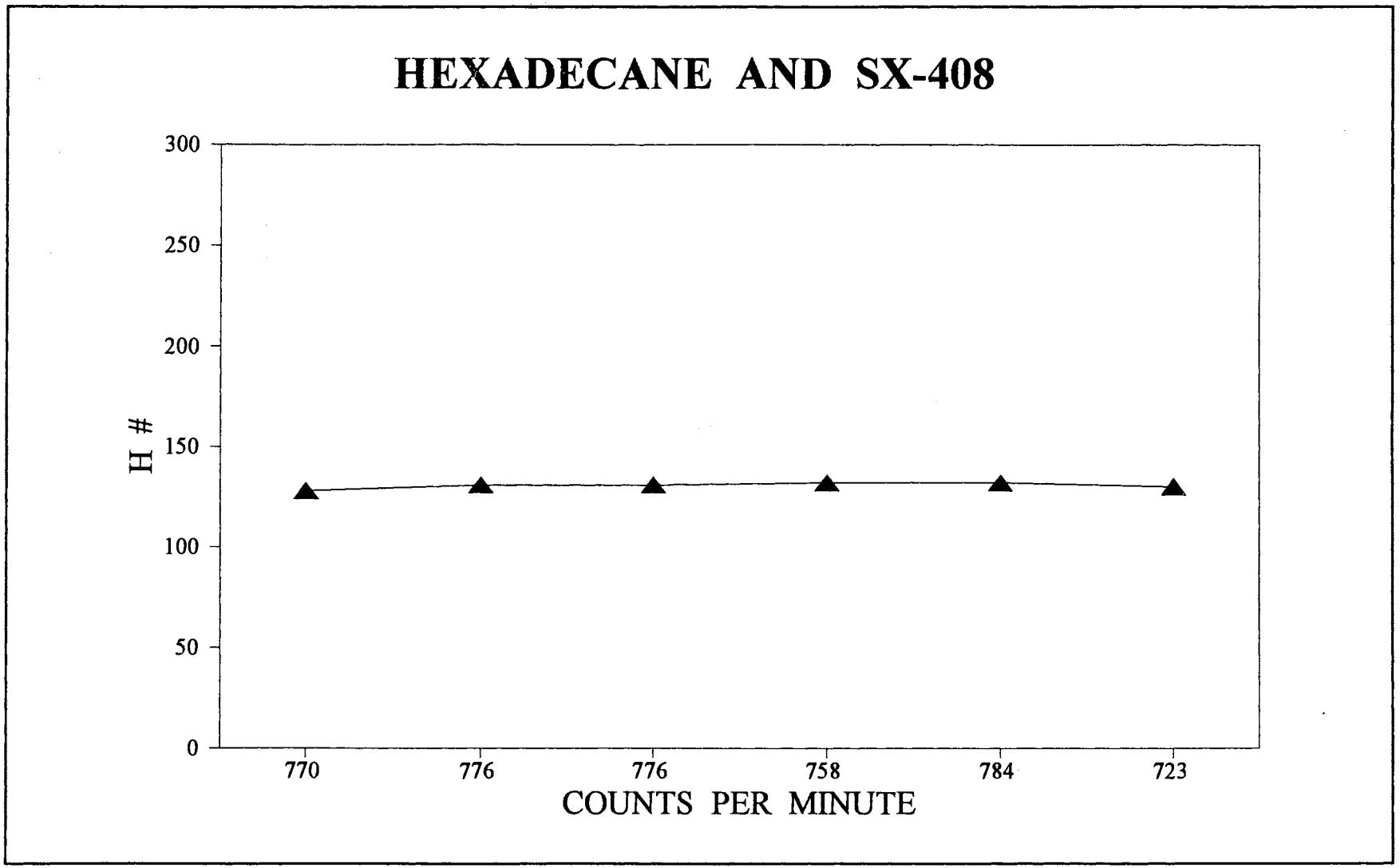

Figure 8. Experimental Quench Curve Example

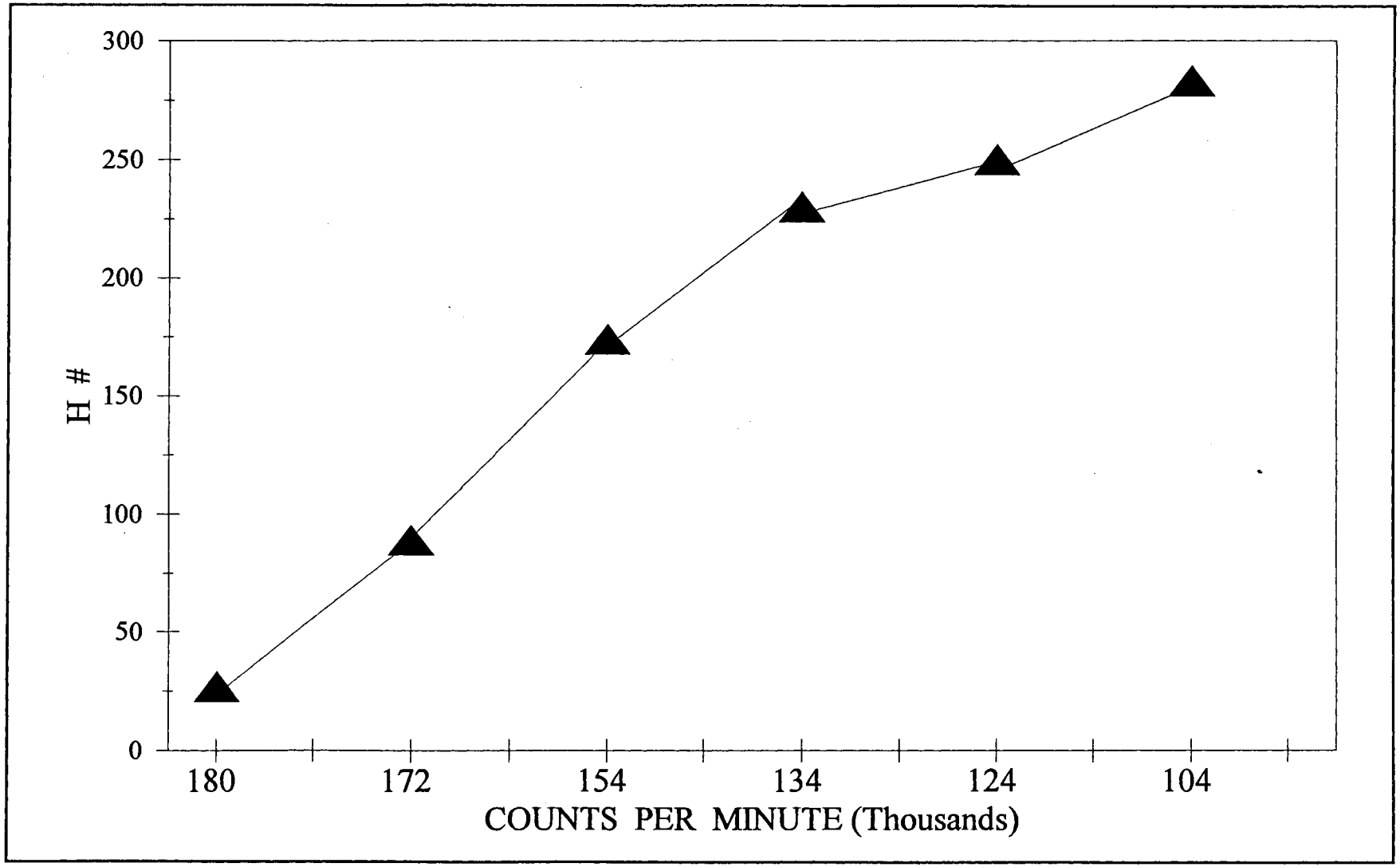

Figure 9. Quench Curve from Standardized Samples

group of surfactant-target compound-target compound concentration interactions (27 total).

Evaporation Loss Studies

For each target compound and at each target compound concentration, experiments were conducted to determine evaporation losses, if any, and the definitive evaporation time. Contaminated vials were evaporated for various time periods and read on the LSC. The resulting data were plotted on time verses disintergrations per minute (DPM) graphs to determine the appropriate evaporation time for each target compound (Figure 10). Exhaust flow rates and evaporation times were adjusted to minimize sample loss.

Soil

The soil selected for this study was collected from terraces one mile south of State Highway 33 on the north side of the Cimarron River in Payne County, Perkins, Oklahoma (139 m E. of SW 1/4 sec. 1, T17N). It had been classified as Psammentic Paleustalfs (Derby) by Gray et al., (1976). The soil was collected from the surface to a depth of one meter. The soil was characterized by the Oklahoma State University Soil Genesis and Morphology Laboratory using the methods described in Table 13. The results of the soil analyses are presented in Table 14. The soil was sieved with a 40 mesh sieve, air dried, mixed and stored in a covered container at ambient laboratory temperatures before use.

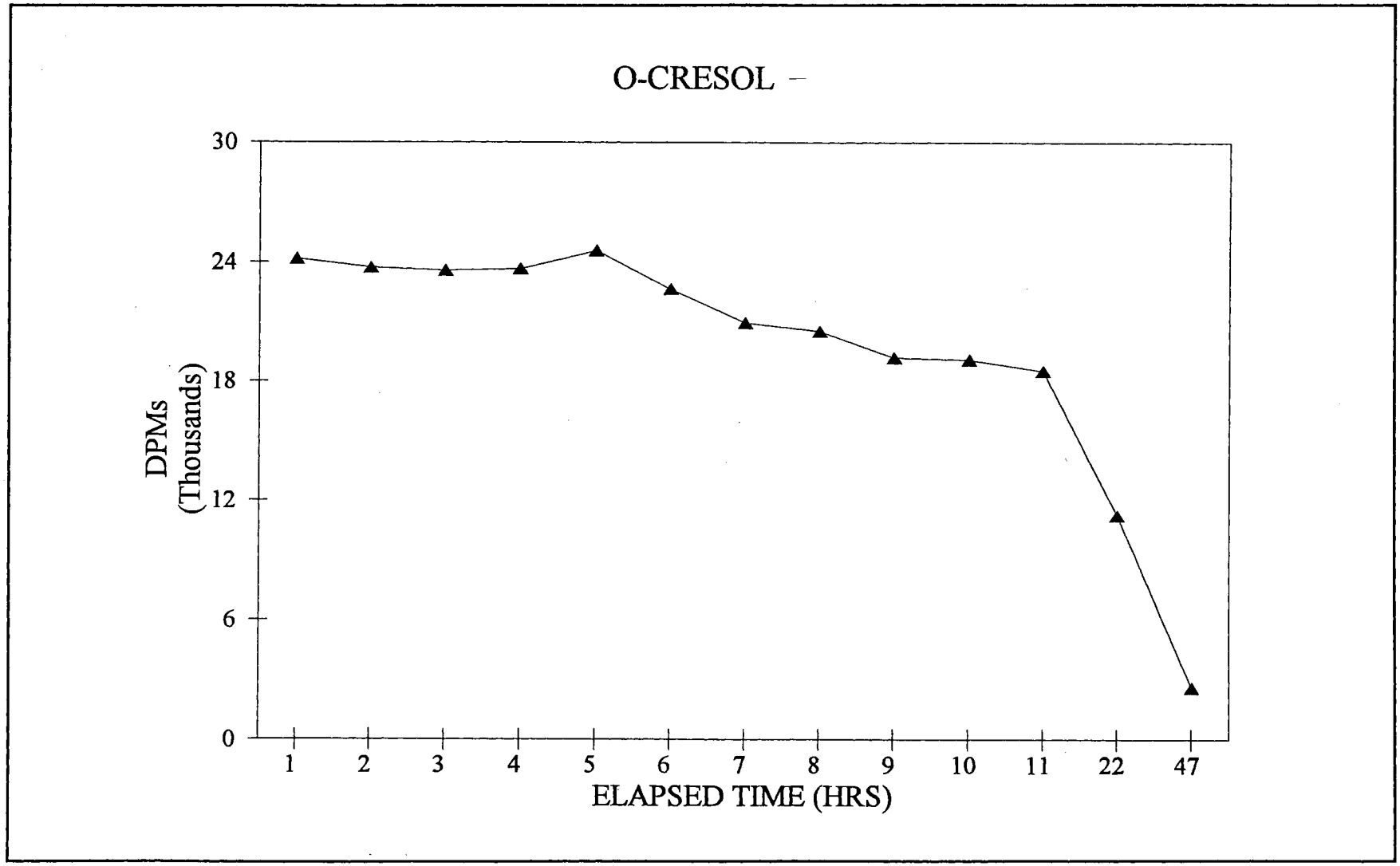

Figure 10. Evaporation Loss Curve Example

TABLE 13

TEST METHODS USED FOR SOIL CHARACTERIZATION

Characterization	Method
Particle Size Analysis	ASA-SSSA, Wet Sieve*
Total Organic Carbon	ASA-SSSA, Walkley-Black
Cation Exchange Capacity	ASA-SSSA Standard Methods (1982)
Surface Area	ASA-SSSA Standard Methods, #16-3.3
Exchangeable Cations	ASA-SSSA Standard Methods (1982)
Exchangeable acidity	ASA-SSSA Standard Methods (1982)
pH	ASA-SSSA, 1:1 Soil:Water
Na	Sodium Acetate Extract, ICP
Ca, K, Mg	Mehlich Extract, ICP

* ASA - American Society of Agronomy, Inc.
SSSA - Soil Science Society of America, Inc.

TABLE 14

CHARACTERIZATION OF EXPERIMENTAL SOIL

Characteristic	Measurement	Recommended*
Total Organic Carbon (%)	0.10	0.5 - 2.0 %
Cation Exchange Capacity (meq/100g)	1.9	
Texture	Loamy -Sand#	Fine to coarse - loamy sand
% Clay	1.1	<18
% Silt	16.9	
% Sand	81.7	>15
Surface Area (m^2/gm)	49.6	
Exchangeable Cations (ppm)		
Ca	276.5	
Mg	70.5	
K	28.5	
Na	43.8	
(Meq/100 G Soil)		
Ca	0.3	
Mg	0.1	
K	0.2	
Na	0.5	
Exchangeable Acidity (Meq/100 G)	0 .8	
Exchangeable Acidity (CMOL/KG Soil)	1.8	
pH	7.0	

* Ellis et al., 1985
# As reported by OSU Soil Genesis Laboratory

Target Compounds

Three environmentally stable hydrophobic organic compounds, which have been identified as residuals in soil at contaminated sites, were selected for the study: hexadecane, o-cresol, and phenanthrene. The criteria for selection included the characteristics which identify a compound as a DNAPL: medium to high octanol/water partition coefficient (K_{ow}), high molecular weight, low vapor pressure, and specific density greater than water. Table 15 lists the physical-chemical characteristics of the target compounds.

The three target compounds represent three groups of hydrocarbons identified at hydrocarbon contaminated sites (Burks, 1981; Ellis et al., 1985; Maguire et al., 1993). The hexadecane represents aliphatic hydrocarbons. The o-cresol represents the alkyl-aromatic group. The phenanthrene represents polynuclear aromatic hydrocarbons. Also, the target compounds were selected, in part, by their availability as ^{14}C labeled representatives of their respective hydrocarbon groups.

The three levels of target compound concentration (TCC) represent similar levels found at waste sites. The three target compound concentrations levels characterize the surfactant behavior with varying concentrations of target compounds.

Surfactants

Three surfactants which have been used as oil dispersants or degreasers were selected for the study; Sandoxylate SX-408, NAXCHEM DISPERSANT K, and

TABLE 15

TARGET COMPOUND PROPERTIES AND ATTRIBUTES

Property	Hexadecane	O-Cresol	Phenanthrene
Formula Weight	226.45	108.13	178.2
Formula	$CH_3(CH_2)_{14}CH_3$	$CH_3C_6H_4OH$	$C_{14}H_{10}$
Melting Point ^0C	20.0	0.9	99-101
Boiling Point ^0C	287.5	191.0	336
Sp. Gravity (g/ml)	0.765	1.0465	1.063
Solubility (in water)	INSOLUBLE	31 ppm @24^0C	INSOLUBLE
Henry's Law Constant (atm-m^3/mol 25^0C)	2.3E + 01	4.7 E-05	2.6E - 05
Log K_{ow}		1.95	4.2-4.6
CAS Registration #	544-76-3	95-48-7	85-01-8
^{14}C Specific Activity (mCi/mmol)	2.2	5.8	8.3
Purity (^{14}C)	> 98%	> 98%	> 98%
Purity (cold)	> 99%	> 99%	> 96%
Supplier (^{14}C)	Sigma	Sigma	Sigma
Supplier (cold)	Sigma	Fisher	Sigma
pK_a		10.2	

InProve (Table 16). The surfactants were provided by the manufacturers in liquid form. For each surfactant, three concentrations of solution were prepared; 0.5%, 1.0%, and 2.0% (v/v). The three concentrations were recommended by the manufacturer or previous investigators cited in the Case Study section.

NAXCHEM DISPERSANT K is used to disperse light, medium and heavy viscosity crude oils in fresh and sea water spills. NAXCHEM K has been used as a cleaner of pumps, pipes, tankwagons, ship tanks, rigs, platforms and other equipment related to the oil industry (Ruetgers-Nease, 1991). It is biodegradable, has low oral toxicity and is functional at 1:40 and 1:80 dilutions with crude oil.

InProve Colloidal Oil Spill Cleanup Agent is listed on the National Contingency Plan product schedule under the category of "dispersants" (Unique Products, Inc., 1991). It has been used *in situ* at oil spill sites on beaches, soil or open fresh or salt water. It was used at the Exxon Valdez spill in Prince William Sound, Alaska. Also, it is used with portable units developed by Unique Products, Inc. for washing of excavated hydrocarbon contaminated soil. The company claims it is 100% biodegradable, nontoxic, and salt tolerant.

Sandoxylate SX-408 has been used in a wide variety of products as a low foaming degreaser and washing detergent; laundry detergents, cosmetics, industrial degreasers and pesticide dispersants (Sandoz, 1986). It has low environmental persistence as it is 73% biodegradable at 21 days.

TABLE 16

SURFACTANT CHARACTERISTICS

Characteristic	SX-408	NAXCHEM K	InProve
Source	Sandoz Chemicals Corp.	Rueters-Nease Chemical Co.	Unique Products. Inc.
CAS #	68439-30-5	Mixture	Mixture
Type	Nonionic & Anionic Mix	Nonionic	Nonionic & Anionic Mix
Chemical Name	Ethoxylated Alcohol	Alkanolamides & Syndets	NA
pH	6.5 (1%)	9 - 10 (1%)	10.4 (Neat)
Purity - %	98	99	99
Bulk Cost	$1.80/lb.	$1.12/lb.	$1.60/gal.*
Specific Gravity	0.97	1.05	1.029
Appearance	Lt. Yellow	Amber	Clear Amber
Trade Name	Sandoxylate SX-408	NAXCHEM DISPERSANT K	InProve

* 8.52 lb./gal

Statistical Analyses

In this section, the statistical analyses are described for each of the hypotheses stated in the introduction. The Systat for Windows (1993) program from Systat, Inc., Evanston, Illinois, was utilized for the analyses.

The data from this experiment consisted of the amount of target compound (mg) desorbed from the contaminated soil (g). From these amounts, a mean or average amount was determined for assorted variables. These mean amounts were then compared with statistical tests to determine if they were different from one another. The assumption being that if they were different from one another, then they had an impact on whether their presence influenced the desorption of the target compound from the soil. A probability (P) of <0.05 indicated that the compared means were statistically different.

For each hypothesis, the means were compared with an Analysis of Variance (ANOVA) and F-test (Table 17). The ANOVA examines the differences between means for each main effect variable and for the interactions of the main effects. With these data, the main effect usually contained three means, e.g., target compound concentrations, surfactant types, etc. A significant main effect indicates that one or more sample means are separated by a sufficient distance that they cannot represent samples drawn from the same population with probability less than 0.05. Significant interactions show mean differences between cells of two or more variables, e.g., a particular target compound by a particular surfactant. Interactions can be either ordinal or disordinal, but when they are present the means are significantly different.

TABLE 17

STATISTICAL TESTS PERFORMED ON DATA

Hypothesis	Test	Variables	Test of Interest	*Post Hoc**
1	4-3 Way ANOVAs	S, TC, TCC, SC, B, pH	S, TC TCC, SC, B, pH	Tukey
2	3 Way ANOVA	S, TC, SC	S*TC	Tukey
3	3 Way ANOVA	S, TC, TCC	S*TCC	Tukey
4	3 Way ANOVA	S, TC, TCC	TC*TCC	Tukey
5	3 Way ANOVA	S, TC, SC	SC*TC	Tukey
6	2-3 Way ANOVAs	S, TC, pH, TCC	pH*S, pH*TC, pH*TCC	Tukey
7	2-3 Way ANOVAs	S, TC, B	B*S, B*TC, B*TCC	Tukey
8-1	3 Way ANOVA	T, TC, TCC,	TC*T	Tukey
8-2	3 Way ANOVA	T, B, TC,	B*T	Tukey
8-3	3 Way ANOVA	T, pH, TC,	pH*T	Tukey
8-4	3 Way ANOVA	T, TC, TCC	TCC*T	Tukey

* If Significant

For example, for TARGET COMPOUND 1 SURFACTANT 1 * TARGET COMPOUND 1 SURFACTANT 2 (hexadecane-NAXCHEM DISPERSANT K*hexadecane-SX-408), if the latter were significant and larger it could said that the surfactant 2 (NAXCHEM DISPERSANT K) removed more hexadecane (target compound 1) than did surfactant 1 (SX-408).

The F-test utilized checked for possible differences in the variable means. This test computed the ratio of mean squares for effect divided by mean squares for the error for degrees of freedom involved in each test. The results of each F-test were associated with an exact probability of the occurrence of an F-ratio of that particular size. Probabilities smaller that 0.05 were considered to be statistically significant. When many comparisons were made and only a few were significant then some may be significant by chance alone.

When ANOVAs wereconducted to test for significant main effects the *post hoc* analyses were used to identify pairwise differences. When the main effect had only two means, the *post hoc* analysis was not necessary. In this case, the significant difference for the main effect was between two means and was determined by inspection. However, when the main effect, e.g. surfactant (S1, S2, S3), had three means, there was uncertainty as to which of the three possible pairs of means (S1-S2, S1-S3, S2-S3) were statistically different. This issue was resolved by means of a *post hoc* analysis, usually a Tukey analysis. This analysis looked at each pairwise comparison of the means and determined whether or not a difference of that size was statistically different. The Tukey *post hoc* also controled for the familywise error rate by dividing the level of significance, typically 0.05, by the number of comparisons

prior to indicating if a comparison was statistically different. This later procedure reduced the risk of specifying a difference significant by chance alone.

Hypothesis 1 tested each of the variables as a main effect. Each of the variables (surfactants, surfactant concentrations, target compounds, target compound concentrations, brines and pHs) was tested to determine if there were any statistically significant differences of the means of the variable levels. All statistical analyses were three-way ANOVAs which tested three main effects per ANOVA.

Hypothesis 2 concerned the impact of the three surfactants on the three target compounds. This SURFACTANT * TARGET COMPOUND interaction, tested with a three-way ANOVA, examined the relationship to determine if the surfactants were differentially effective in removing the Target compounds.

Hypothesis 3 dealt with the influence of three levels of target compound concentrations on the surfactants' desorption of the target compounds and was tested by the interaction TARGET COMPOUND * TARGET COMPOUND CONCENTRATION in a three-way ANOVA. Three different surfactants were tested to determine if target compound concentration levels are a significant design parameter for remediation systems.

Hypothesis 4 concerned the impact of target compound concentration on the desorption of target compounds and was tested by the interaction TARGET COMPOUND * TARGET COMPOUND CONCENTRATION in a three-way ANOVA. This interaction determined if target compounds were differentially removed at different concentration levels.

Hypothesis 5 concerned the influence of surfactant concentrations of each surfactant on the effectiveness of a remediation system. The SURFACTANT * SURFACTANT CONCENTRATION interaction was tested with a three-way ANOVA. These results may have important economic system design and performance optimization implications.

Hypothesis 6 dealt with the impact of three possible ground water pH levels on contaminant desorption and was tested by the SURFACTANT * pH, TARGET COMPOUND * pH, and TARGET COMPOUND CONCENTRATION * pH interactions. The SURFACTANT* pH interaction examined the relationship between the surfactants and pH levels. This test determined if one surfactant was more effective than the others for desorbing contaminants at certain pH levels. The TARGET COMPOUND * pH interaction ascertained if the target compounds behaved differently at various pH levels. The TARGET COMPOUND CONCENTRATION * pH interaction delineated the influence of target compound concentrations at varying pH levels. Each interaction was drawn from a three-way ANOVA.

Hypothesis 7 dealt with the impact of three possible ground water levels of brine on desorption and was tested by the interactions SURFACTANT * BRINE, TARGET COMPOUND * BRINE and TARGET COMPOUND CONCENTRATION * BRINE. The SURFACTANT* BRINE interaction had implications for the choice of the most effective surfactant(s) for various possible on site brine conditions. The TARGET COMPOUND * BRINE interaction examines the relationship of the target compound at various brine levels in relationship to the amount of target compound desorbed. The TARGET COMPOUND CONCENTRATION * BRINE interaction

delineated the relationship of possible site target compound concentrations and possible levels of site brine conditions and their effects on the removal of the contaminants. Each interaction was drawn from a three-way ANOVA.

Hypothesis 8 concerned the relationship of the flush types (TYPE 1 = surfactant flushes, TYPE 2 = water flushes) across the study variables by the interactions of TYPE * TARGET COMPOUND, TYPE * TARGET COMPOUND CONCENTRATION, TYPE * pH, TYPE * BRINE, as well as for the main effect for TYPE. The TYPE* TARGET COMPOUND interaction examined the relationship to determine if surfactants overall were more effective than water in flushing the individual target compounds from the soil. The TYPE * TARGET COMPOUND CONCENTRATION interaction delineated the influence of the two flush types on the effectiveness of the respective systems in removing target compounds from varying target compound concentraion levels. The TYPE * pH and TYPE * BRINE interactions inspected the influence of the possible levels of ground water pH and brine on the two types of flushes. The main effect of type (T) was examined to indicate whether surfactant flushes were overall more effective than water flushes in removing all the target compounds from the soil. Each of the interactions and the main effect for type was drawn from a three-way ANOVA.

CHAPTER IV

RESULTS AND DISCUSSION

Soil Characterization

The soil characterization analyses defined a loamy sand soil with a neutral pH and low organic carbon content (Table 14, chapter 3). This type of soil is recommended for soil flushing as it has a medium to high hydraulic conductivity (10^{-2} to 10^{-4} cm/sec) to allow free movement of water and low organic carbon to minimize sorption of the surfactants and target compounds. The characteristics of the selected soil meet the criteria previously mentioned and established by Ellis et al. (1985) for the suitable soil type to be used with *in situ* surfactant enhanced soil flushing.

Shaker Equilibrium Batches

Shaker equilibrium batches were run for combinations of target compound, target compound concentration, surfactant, and surfactant concentration. The longest equilibrium time was determined to be 5-6 hours for hexadecane. O-cresol and phenanthrene equilibrium times were 1 hour with no change over 24 hours. Therefore, all reactor vials were shaken for 6 hours to maintain continuity in the experimental procedure.

Quench Determination

Quench curves were plotted with data from 27 different surfactant-target compound-target compound concentration combinations. There was no quenching in any of the various solutions. Therefore, the data did not need to be corrected and were used as read from the LSC.

Statistical Analyses

All the data tables presented henceforth are located in the Appendix. In the following section each hypothesis is presented. The data analyses for that hypothesis are discussed including ANOVA, means and Tukey test pairwise mean differences tables (when the results are significant), and the results interpreted. Since the Tukey tests were run to compare pairwise mean differences of significant variables, if the variables were proven not significant in the ANOVA, no Tukey test was performed. The Tukey pairwise differences are presented in a half rectangular array. The differences are aligned in pairs based on their placement in the array. The majority of the differences are significant; the non-significant pairwise differences are indicated with an asterisk. At the end of the chapter, additional components of the existing statistical analyses, which were not related to the hypotheses, but which were significant, are reported.

Hypothesis #1 concerned the main variables individually. The subsequent hypotheses related to the interactions of the various main variables.

Hypothesis 1

The first hypothesis individually examined the various main effects, or the main variable of interest: surfactants, surfactant concentrations, target compounds, target compound concentrations, pHs and brines. There were three levels of each main variable. Hypothesis 1 stated that there are no differences between the levels of each main variable listed above in terms of milligrams of target compound desorbed from the soil.

A summary of the various main effect test results (Table 18) indicate that the amounts of the target compound desorbed from the soil for the main effect variables of pH and brine were not significant. Hence, the pH and/or brine levels did not affect the sorption of the target compounds. Therefore, the corresponding null hypotheses for the main effect variables of pH and brine were not rejected. The problems previously identified by Gannon et al., (1989) and Fountain (1992) (decreased surfactant effectiveness with increased brine concentration) were not experienced under the conditions and variables used in this study. All the other main variables were statistically significant and affected the desorption of the target compound from the soil. The associated means and standard deviations of the amount of target compounds desorbed for each of the main variables for Hypothesis 1 are presented in Table 19. Table 20 presents the Tukey *post hoc* test results for Hypothesis 1, which compared the mean concentrations from Table 19. Each main variable, or main effect, will be discussed separately.

Hypothesis 1A - Main Effect of Surfactants. Hypothesis 1A stated that there were no differences between the three surfactants in terms of the milligrams of all target compounds desorbed from the soil under all other variable conditions. An examination of the mean amounts of target compound desorbed by the individual surfactants shows that SX-408 (S1) promotes or facilitates more desorption (6.322 mg/g or 68%) than does S2, NAXCHEM DISPERSANT K, (5.672 mg/g or 61%) or S3, InProve (5.283 mg/g or 57%) (Table 19 and Figure 11). Table 21 presents the three-way analysis of variance for surfactants, target compounds, and target compound concentrations variables. This analysis showed that for the surfactant variable (S) there was a significant difference between surfactants ($P < 0.05$). Table 20 indicates there was a significant difference between S1 and S3 (SX-408 and InProve), but not between S1 and S2 (SX-408 and NAXCHEM DISPERSANT K) or S2 and S3 (NAXCHEM DISPERSANT K and InProve). Because the overall difference was significant, this hypothesis was rejected.

Of the three surfactants tested, Sandoxylate SX-408 (S1) would be the surfactant of choice at waste sites contaminated with compounds with physical/chemical characteristics similar to the target compounds tested. Although their mean amount desorbed was less than SX-408, the NAXCHEM DISPERSANT K and the InProve desorbed impressive amounts of the target compounds as well. Economic differences between the surfactants may be the deciding factor for use.

Hypothesis 1B - Main Effect of Surfactant Concentrations. Hypothesis 1B, in the null form, stated that the surfactant concentration does not make a difference in terms of the amount of target compound (mg) desorbed from the soil. The ANOVA

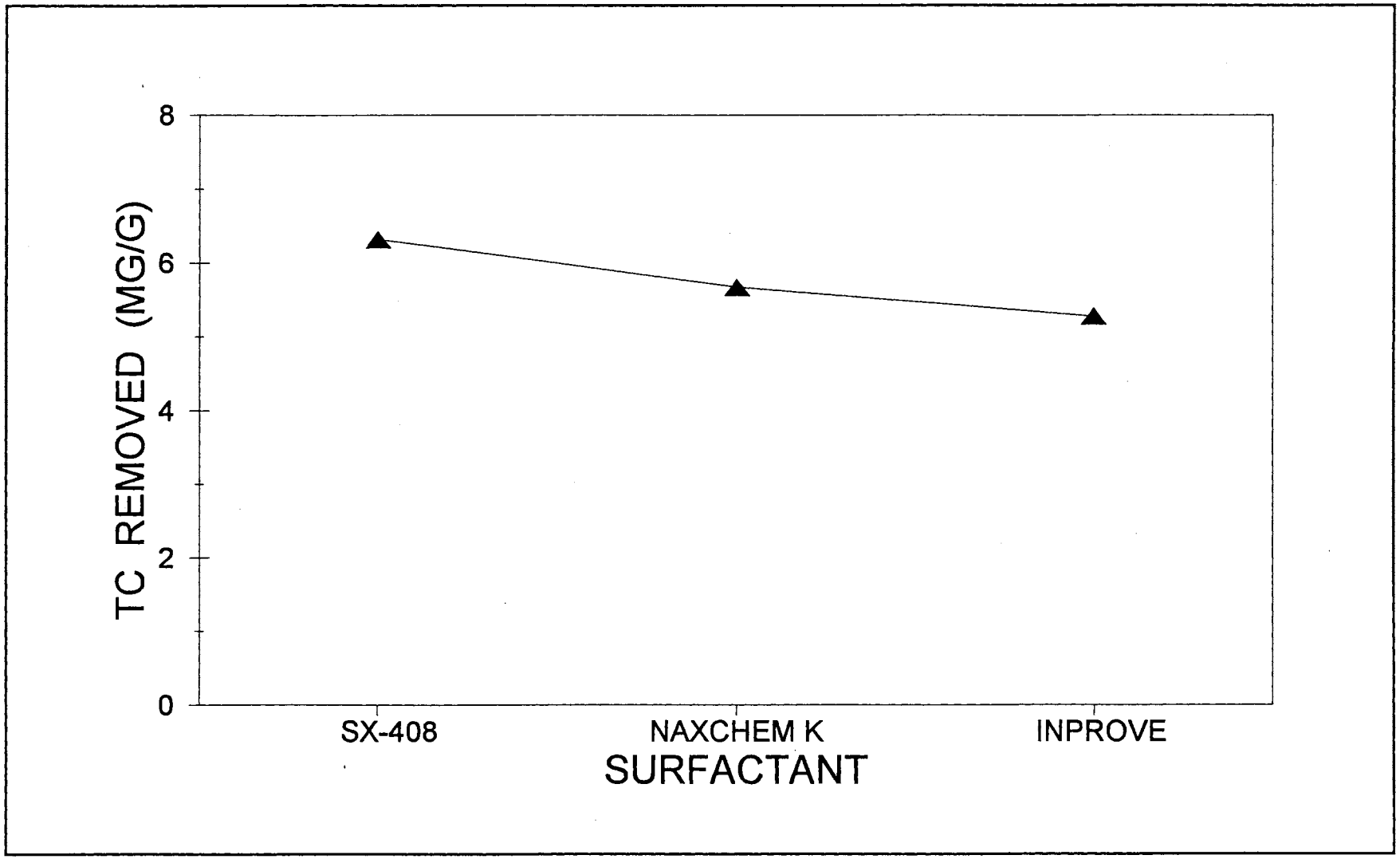

Figure 11. Average Amount of All Target Compounds Removed by Each Surfactant (Hypothesis 1A, Table 19)

data for target compounds for all surfactants and surfactant concentrations indicate that there was a significant difference ($P < 0.05$) between the amount of target compound desorbed at different surfactant concentrations (Table 21). Therefore, the hypothesis was rejected.

An examination of the means of the amount of target compound desorbed at each surfactant concentration presented in Table 19 and Figure 12 shows that for surfactant concentration, the overall lowest amount of target compound desorption took place in SC1 (0.5% surfactant concentration) batches (5.037 mg/g). For overall target compound desorption, the SC2 (1% surfactant concentration) batches removed 5.901mg/g and the SC3 (2% surfactant concentration) batches removed 6.339 mg/g . The differences between the 0.5% (SC1) and 1.0% (SC2) were significant as were the differences between 0.5% (SC1) and 2.0% (SC3). However, the difference between 1.0% and 2.0% was not significant (Table 20). Economic considerations would favor the use of the 1% surfactant solution since the cost would be half as much. These data indicate that the surfactant concentration is a significant design parameter and economic consideration for ISSSF remediation systems.

Hypothesis 1C - Main Effect of Target Compounds. Hypothesis 1C stated, in the null form, that there were no differences between the three target compounds in terms of the amount desorbed from the soil when the surfactant solutions are treated as a single variable. The analysis of variance data for the main effect of target compound (Table 21), indicates that the target compound variable was significant; thus the hypothesis was rejected. *Post hoc* test data (Table 20) indicate that there were no differences in the removal between o-cresol and hexadecane but there were

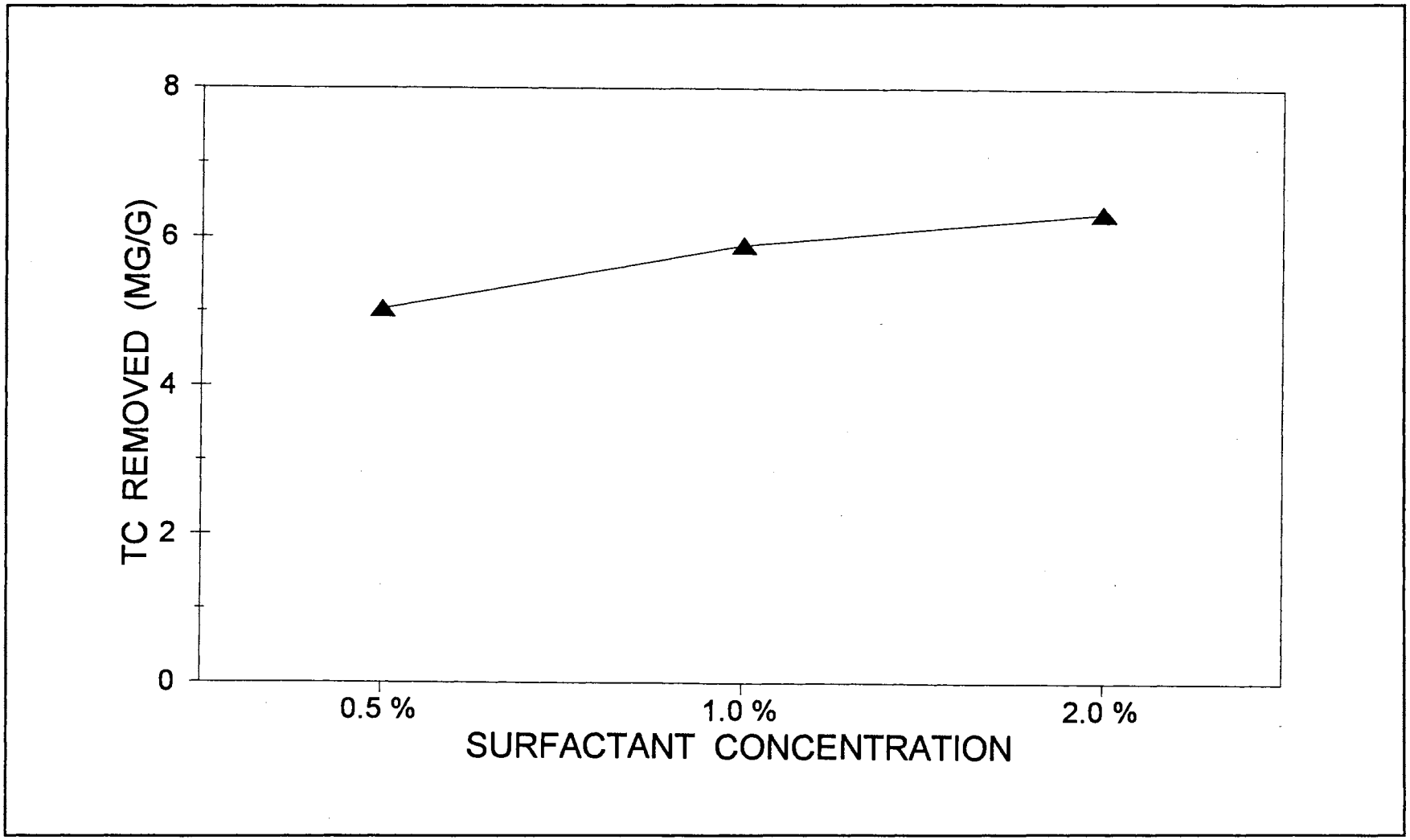

Figure 12. Average Amount of All Target Compounds Removed at Each Surfactant Concentration of All Surfactants (Hypothesis 1B, Table 19)

significant differences between both of those contaminants and phenanthrene, with phenanthrene being the least desorbed.

The semi-volatile compound o-cresol has a higher solubility than the other compounds and would be expected to be more easily desorbed (Table 15). The average amount of target compound desorbed support that assumption and indicate the desorption of the target compounds from the soil as follows: o-cresol (7.011 mg/g), hexadecane (6.976 mg/g) and phenanthrene (3.290 mg/g) (Table 19 and Figure 13). Hexadecane and o-cresol desorbed and average amount twice that of phenanthrene. The difference between o-cresol and hexadecane was not significant (Table 20). Transferring these data to the compound groups represented by the target compounds would indicate the order of desorption from soils at contaminated sites to be alkylaromatic and aliphatics > PAHs. Synergistic effects among target compounds, however, were not assessed in this study as each target compound was tested independently.

Hypothesis 1D - Main Effect of Target Compound Concentrations.

Hypothesis 1D, stated in the null form, proposed that there are no differences between target compound concentrations in terms of the amount of target compound (mg) desorbed from the soil when target compounds and surfactants are treated as single variables. Table 22 presents the three-way analysis of variance data for surfactant type, target compound and target compound concentration variables. This analysis indicates that there were significant differences between target compound concentrations ($P < 0.05$).

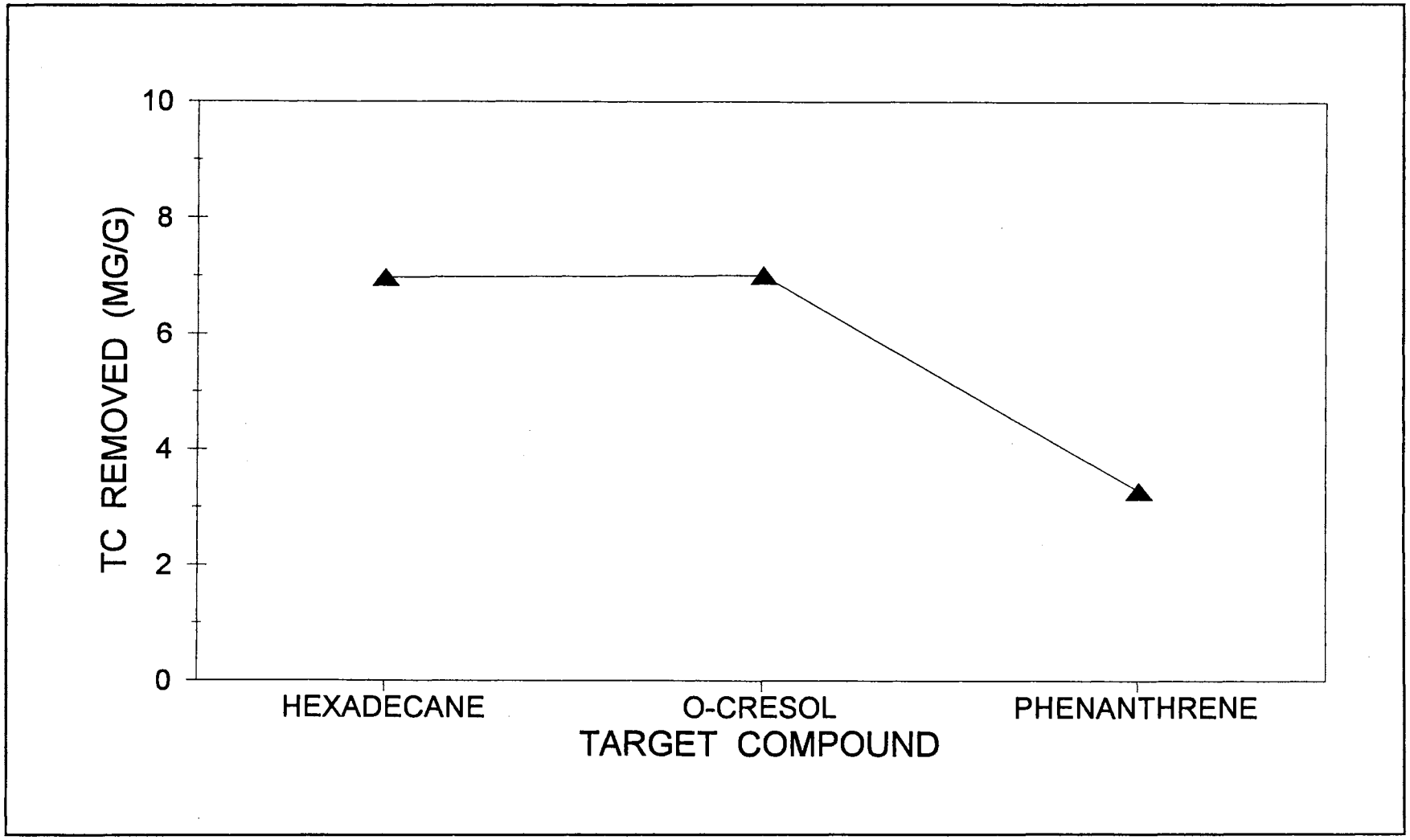

Figure 13. Average Amount of Target Compound Removed for Each Target Compound (Hypothesis 1C, Table 19)

An examination of the means of the amount of target compound desorbed shows that for target compound concentrations, TCC1 had the lowest amount of target compound desorbed (3.076 of 4.620 mg/g), followed by TCC2 (5.351 of 9.240 mg/g) and TCC3 (8.851 of 13.860 mg/g), respectively (Table 19 and Figure 14). Comparing these mean amounts to each other shows that each of the three sets of these pairwise mean differences was significant (Table 20). Therefore, this hypothesis was rejected as there were significant differences in the amount of target compound desorbed in the different target compound concentrations.

Ranking the target compound concentration levels as percent desorbed from highest to lowest is as follows: TCC1 (66.6%), TCC3 (63.9%) and TCC2 (57.9%). Transferring that information to the field would translate that a finite amount of the contaminant can be solubilized per flush. Additional removal would require additional flushes. These data are supported by the multiple flush system for heavy DNAPL contamination in the field study of Sale and Pitts (1989).

Hypothesis 1E - Main Effect of pHs. Hypothesis 1E, in the null form, stated that the pH level of the flushing solution does not make a difference in terms of the amount of target compound flushed from the soil. The three-way ANOVA data for the pH, target compound, and surfactant variables show that there were no significant differences for pH, or for pH * TARGET COMPOUND, or for pH * SURFACTANT (Table 23). Therefore, this hypothesis was not rejected.

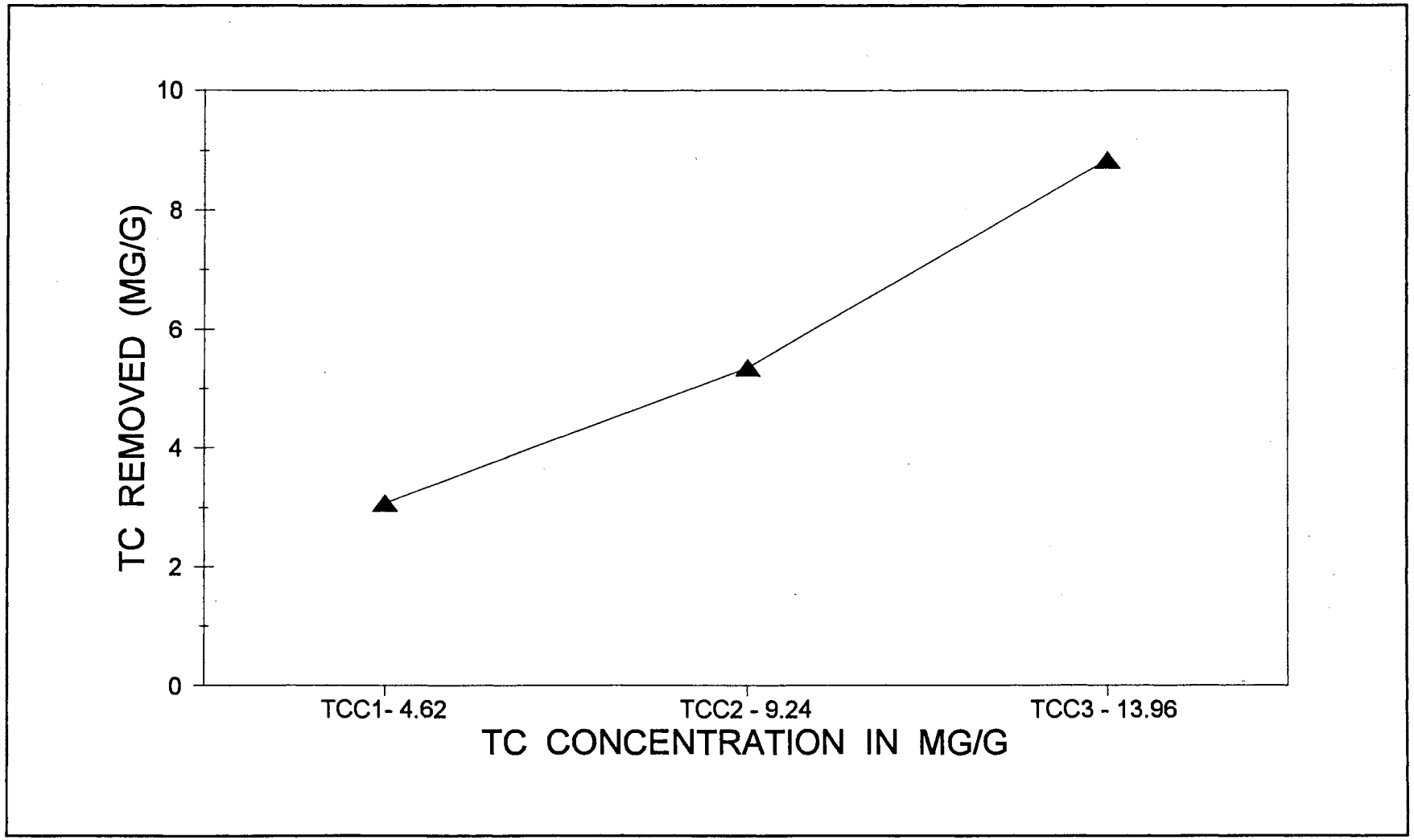

Figure 14. Average Amount of All Target Compounds Removed at Each Target Compound Concentration (Hypothesis 1D, Table 19)

The means and standard deviations of the amount of target compound desorbed for this test, pH1 (5.818 mg/g, SD = 3.581, pH2 (5.954 mg/g, SD = 3.710) and pH3 (5.506 mg/g, SD = 3.522), indicate that the pH in the 5.5 to 8.5 range was not a significant factor in the effectiveness of the tested surfactants to desorb the target compounds from the soil (Table 19 and Figure 15). However, a trend of decreasing adsorption as the pH moves in either direction from neutral pH (7) may be implied by a comparison of the three means.

Hypothesis 1F - Main Effect of Brines. Hypothesis 1F stated that the brine concentration of the flushing solution does not make a difference in terms of the amount of target compound (mg) desorbed from the soil. The analysis of variance for the interaction of the brine, surfactant and target compound variables indicates that there were no significant differences between BRINE, BRINE * TARGET COMPOUND and BRINE * SURFACTANT (Table 24). Therefore, this hypothesis was not rejected.

The TC desorbed means for BRINE1 (6.524 mg/g), BRINE2 (6.521 mg/g) and BRINE3 (6.463 mg/g) did not indicate a significant difference in the amount of target compound desorbed from the soil (Table 19 and Figure 16). The NAXCHEM DISPERSANT K and the InProve have been used for oil spills in marine environments. These data confirm the brine tolerance of these surfactants to marine conditions. It now appears that these surfactants would perform in fresh and brackish waters as they do in the saline marine environment.

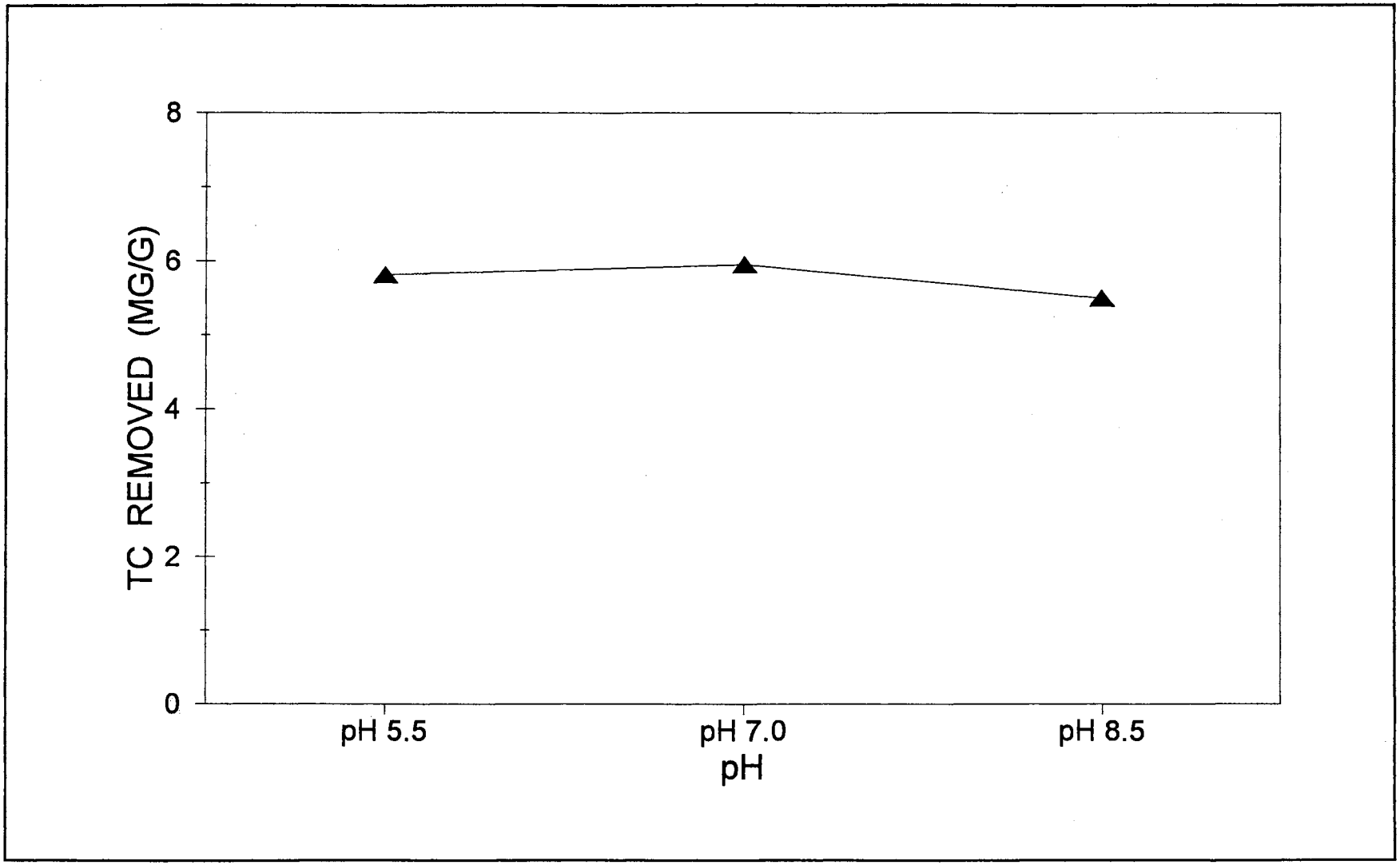

Figure 15. Average Amount of All Target Compounds Removed at Each pH (Hypothesis 1E, Table 19)

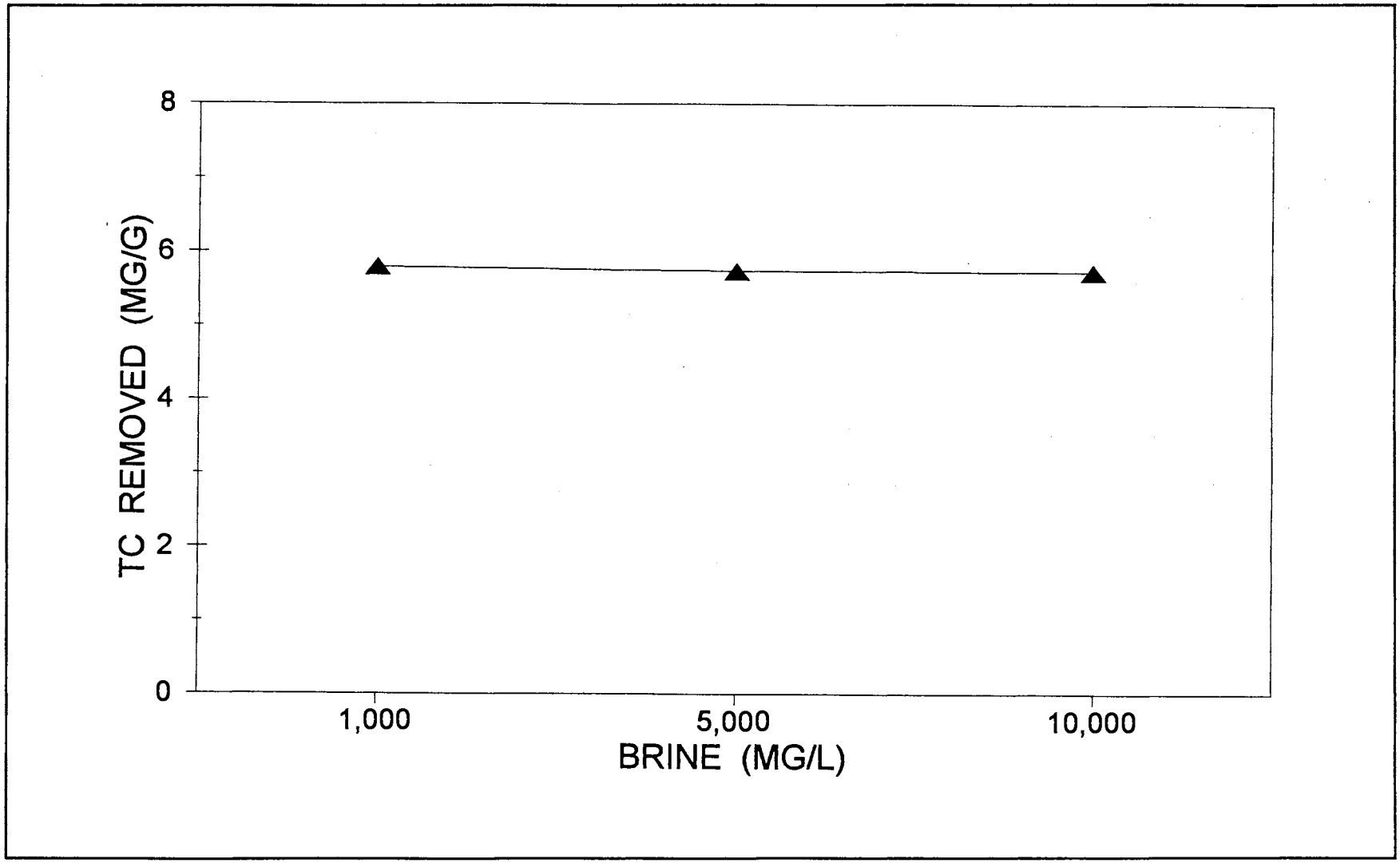

Figure 16. Average Amount of All Target Compounds Removed at Each Brine Level (Hypothesis 1F, Table 19)

Hypothesis 2

The second hypothesis, stated in the null form, said that when using each surfactant, there is no difference between target compounds in terms of mg of target compound desorbed from the soil. The analysis of variance data containing the interaction of SURFACTANT *TARGET COMPOUND indicate that the interaction was significant (Table 21). The hypothesis was, therefore, rejected.

The pairwise means and the *post hoc* test data indicate that thirty four of the thirty-six pairwise comparisons were significant (Tables 25 and 26). The means and Figure 17 indicate that for hexadecane, the best target compound removal was obtained with SX-408 (S1) followed by InProve (S3) and NAXCHEM DISPERSANT K (NAXCHEM K or S2), in that order. For the target compound o-cresol, the best removal was obtained with InProve followed by NAXCHEM K and SX-408, in that order. For phenanthrene, the best removal was obtained by SX-408 followed by NAXCHEM K and InProve, in that order. Phenanthrene was the least flushable target compound while hexadecane and o-cresol were quite similar in their response to flushing. Hence the individual surfactants perform differently with the individual target compounds.

Hypothesis 3

Hypothesis 3 stated that for each surfactant there are no differences between target compound concentrations in terms of mg of target compound desorbed from the soil. The analysis of variance with the interaction term SURFACTANT * TARGET

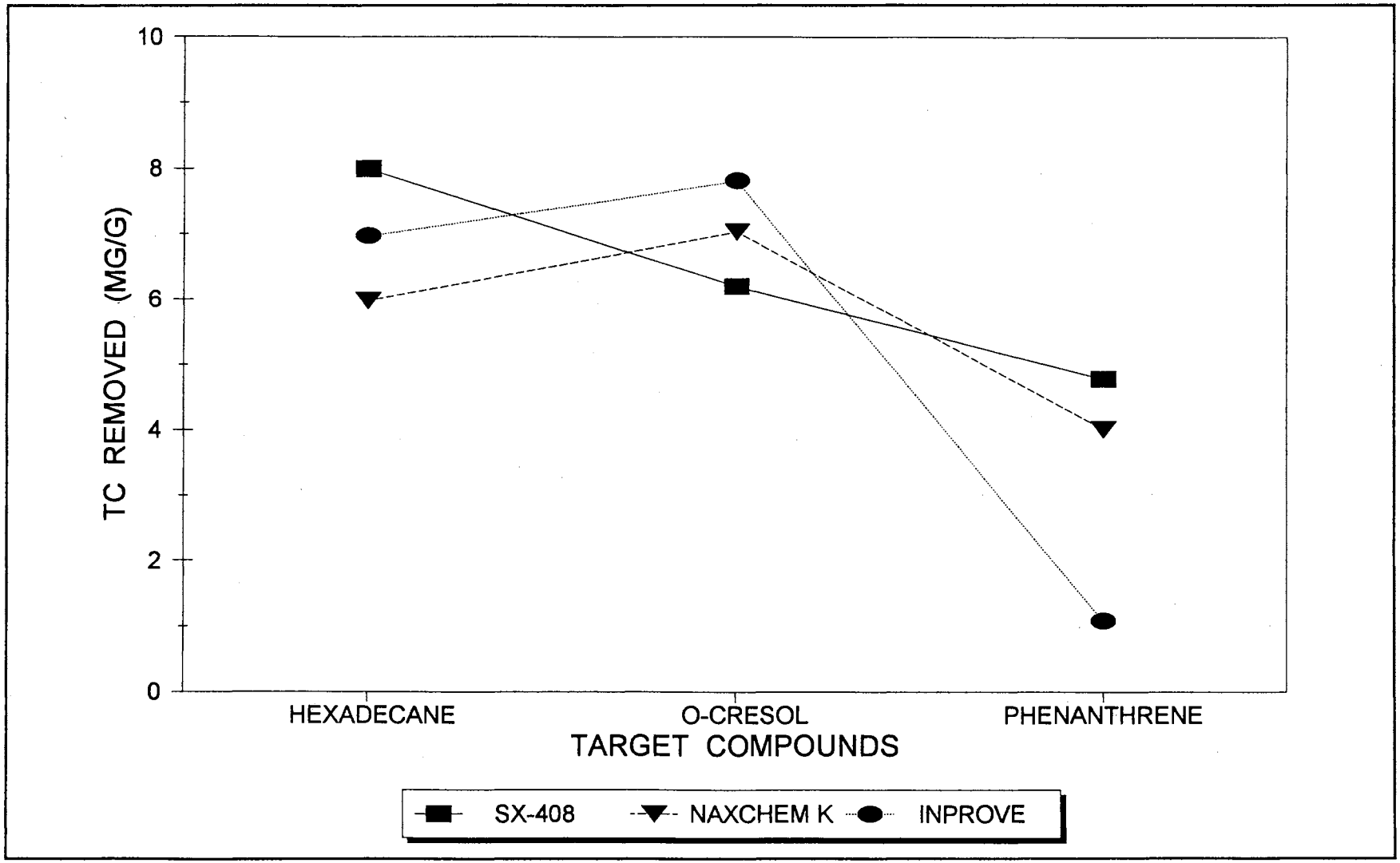

Figure 17. Average Amount Each Target Compound Removed for Each Surfactant (Hypothesis 2, Table 25)

COMPOUND CONCENTRATION indicates that the interaction was significant and therefore hypothesis 3 was rejected (Table 22).

The means and Tukey test data for the SURFACTANT * TARGET COMPOUND CONCENTRATION interaction indicated that 32 of 36 pairwise mean comparisons were significant (Tables 27 and 28). As the target compound concentrations increased, the standard deviation of the averages increased. TCC1 had the lowest amount of target compound removal followed by TCC2 and TCC3 for all surfactants (Figure 18). Hence the CMC was not exceeded with the concentrations used. Surfactant 1 (SX-408) was the most effective at removing the contaminants at all three target compound concentrations. For TCC1, only 1 pair of averages was significantly different, SX-408 - NAXCHEM K (S1-S2) PAIR. For TCC2 only the NAXCHEM K - InProve (S2-S3) pair was not significantly different. For TCC3, the SX-408 - NAXCHEM K (S1-S2) pair was not significantly different. The greatest difference at any one target compound concentration is 1.35 mg/g at TCC3 for the SX-408 - InProve (S1-S3) pair. This difference may not be an economically or practically significant difference although it is a statistically significant difference.

Hypothesis 4

Hypothesis 4 stated that for each target compound there are no differences in target compound concentration in terms of mg of target compound desorbed from the soil. The analysis of variance with the TARGET COMPOUND * TARGET COMPOUND CONCENTRATION interaction indicates that the interaction was highly significant, therefore the hypothesis was rejected (Table 22). The pairwise

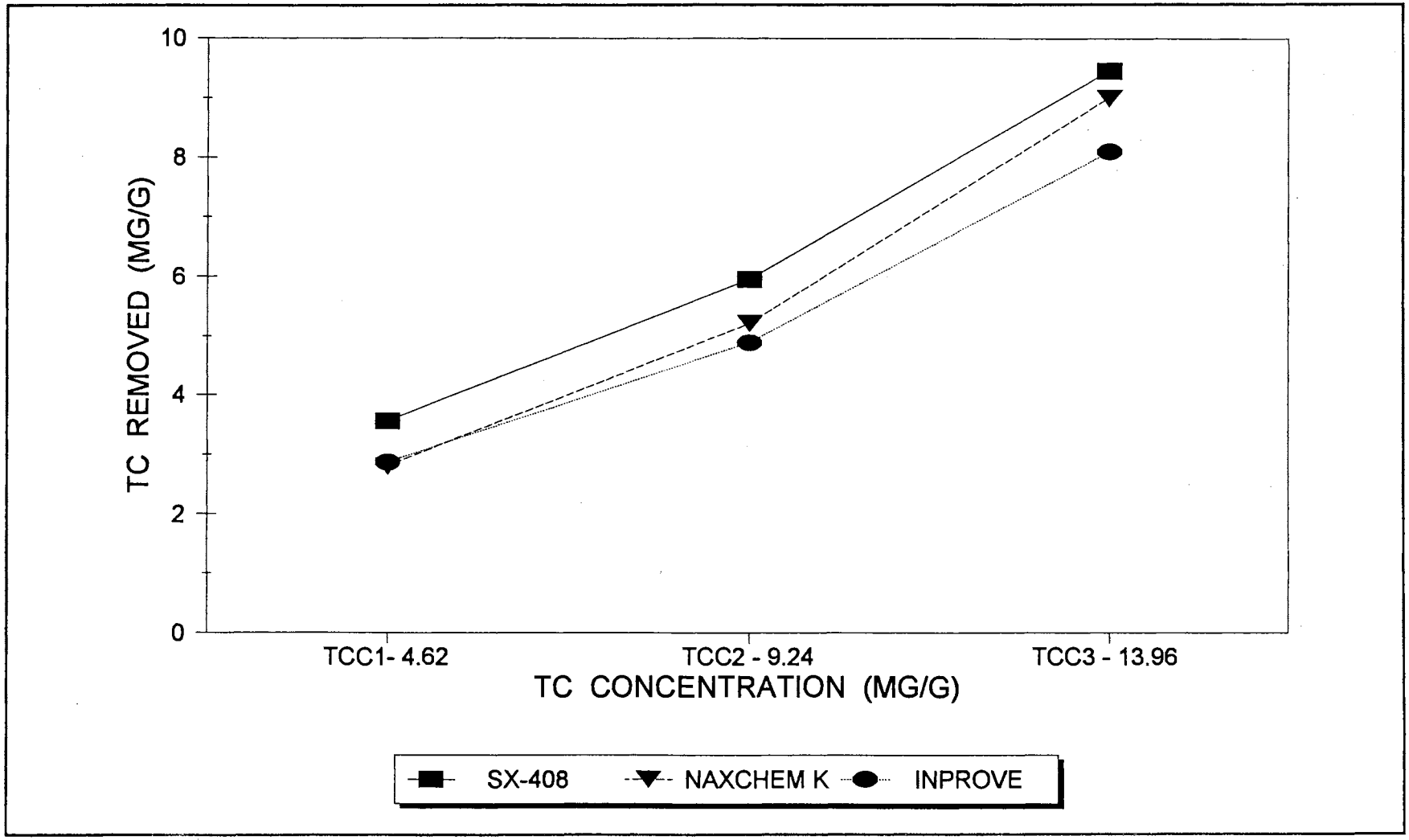

Figure 18. Average Amount of All Target Compounds Removed at Each Target Compound Concentration with Individual Surfactants (Hypothesis 3, Table 27)

means and Tukey test data indicate that 32 of the 36 pairwise comparisons were significant (Tables 29 and 30). Phenanthrene was statistically different from hexadecane and o-cresol at all target compound concentrations. Between TCC2 and TCC3 the mg of target compound removed doubled. These data have implications relating to the expected recovery of high concentrations of PAHs in soil.

Target compound concentration 1 (4.62 mg/g) had the lowest desorption amount and no significant differences among the target compounds (Figure 19). Target compound concentration 3 (13.86 mg/g) had the highest desorption across all three target compounds. There was a difference between the first two target compounds (hexadecane and o-cresol) and the third target compound (phenanthrene) at all the concentrations, again, reflecting the very low solubility of phenanthrene.

Hypothesis 5

Hypothesis 5 states that the surfactant concentration of each surfactant across all target compounds does not make a difference in terms of the mg of target compounds desorbed from the soil. The analysis of variance data for the SURFACTANT* SURFACTANT CONCENTRATION interaction used to test this hypothesis indicates that the interaction was not significant (Table 21). Hypothesis 5 was, therefore, not rejected. The lack of differences between the variable means is shown in Table 31 and Figure 20. For surfactant concentration 1, the means were so closely grouped (5.091, 5.039, and 4.982 mg/g) that their symbols overlap and appear as one.

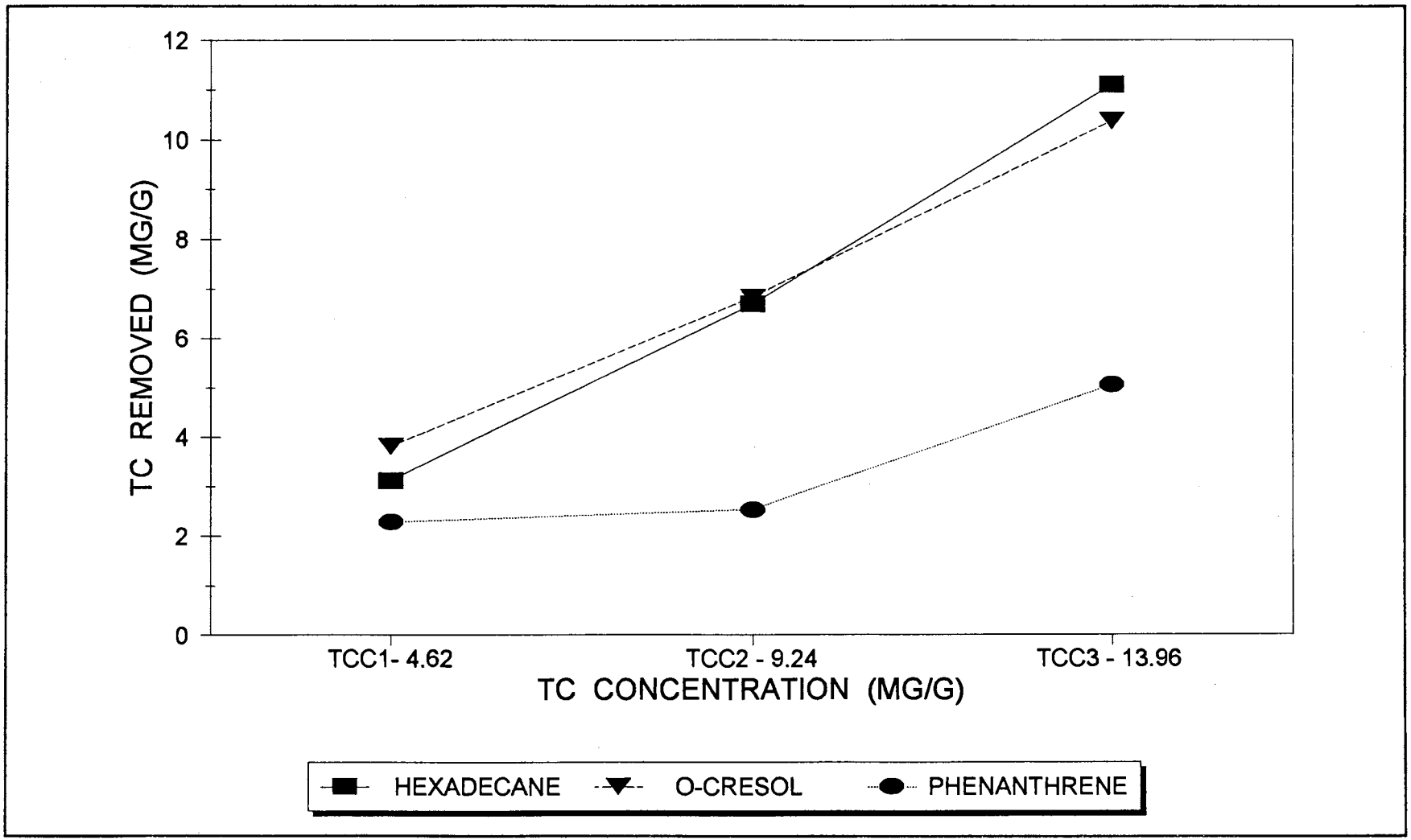

Figure 19. Average Amount of the Target Compounds Hexadecane, O-Cresol and Phenanthrene Removed at Each Target Compound Concentration (Hypothesis 4, Table 29)

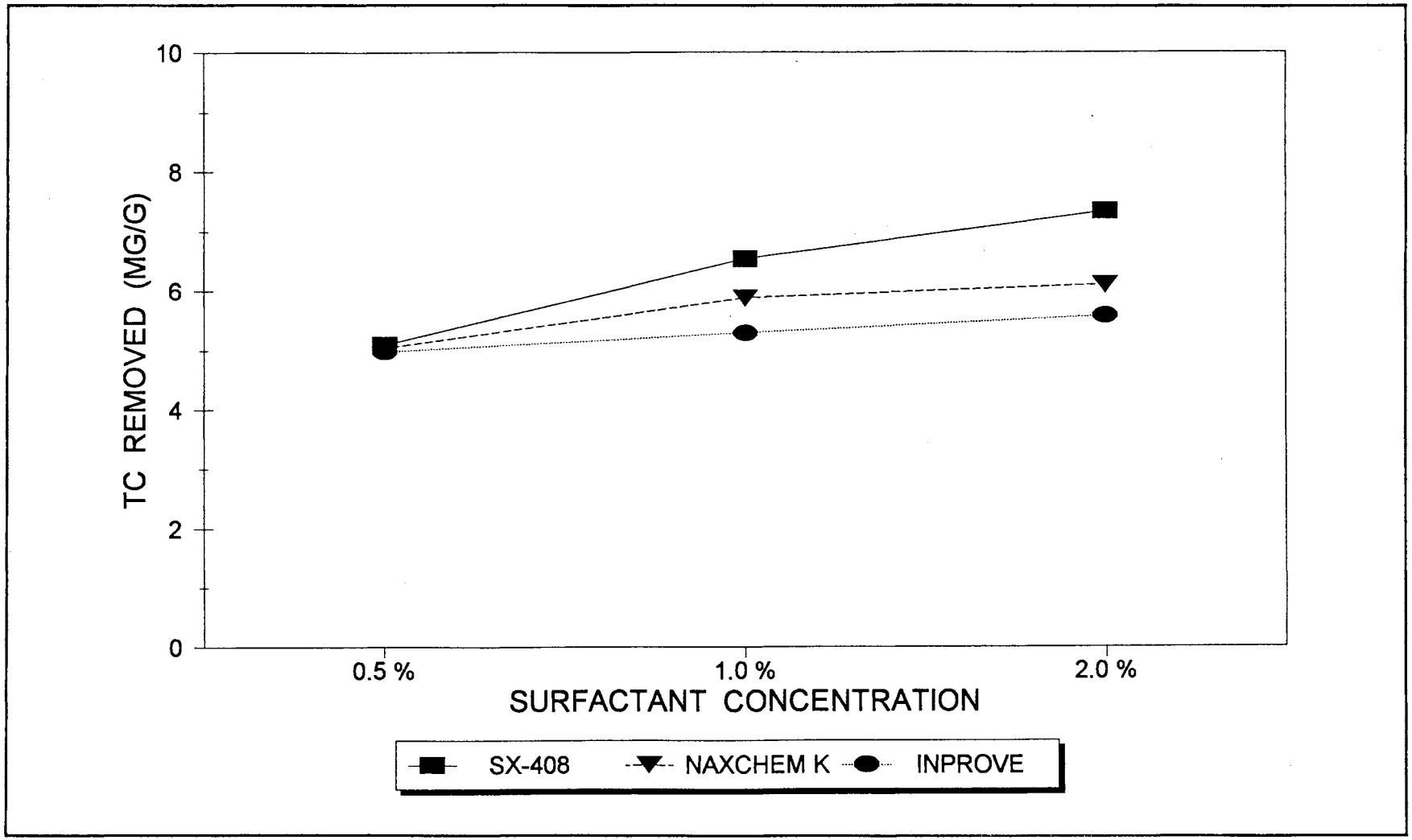

Figure 20. Average Amount of All Target Compounds Removed by the Surfactants SX-408, NAXCHEM K and INPROVE at Each Surfactant Concentration (Hypothesis 5, Table 31)

Hypothesis 6

Hypothesis 6 concerns pH and its impact on several variables. The null hypothesis states that the pH level of the flushing solution for all surfactant types or target compounds or target compound concentrations does not make a difference in terms of the mg of target compound flushed from the soil. The interactions of SURFACTANT* pH, TARGET COMPOUND * pH and TARGET COMPOUND CONCENTRATION *pH were not significant (Tables 23 and 32), therefore the hypothesis was not rejected. The SURFACTANT * pH averages from Table 33 are presented in Figure 21. Figure 22 presents the TARGET COMPOUND * pH means from Table 34. Hexadecane (TC1) and o-cresol (TC2) are plotted in almost exactly the same space. The apparent differences in Figure 22 represent only differences in the individual target compound solubility, but indicate no changes at different pH levels. Figure 23 presents the TARGET COMPOUND CONCENTRATION * pH interaction means from Table 35. The straight lines in the figures indicate the small standard deviations in the means for each target compound concentrations for all pHs. There are significant differences, however, between the target compound concentrations as displayed on the graph by three separate almost parallel lines.

Hypothesis 7

In the null form, hypothesis 7 states that the brine concentration of the flushing solution across the following variables is not a significant factor in removing the target compounds from the soil: surfactants, target compounds, and target compound concentrations. The data from the ANOVAs of the SURFACTANT * BRINE,

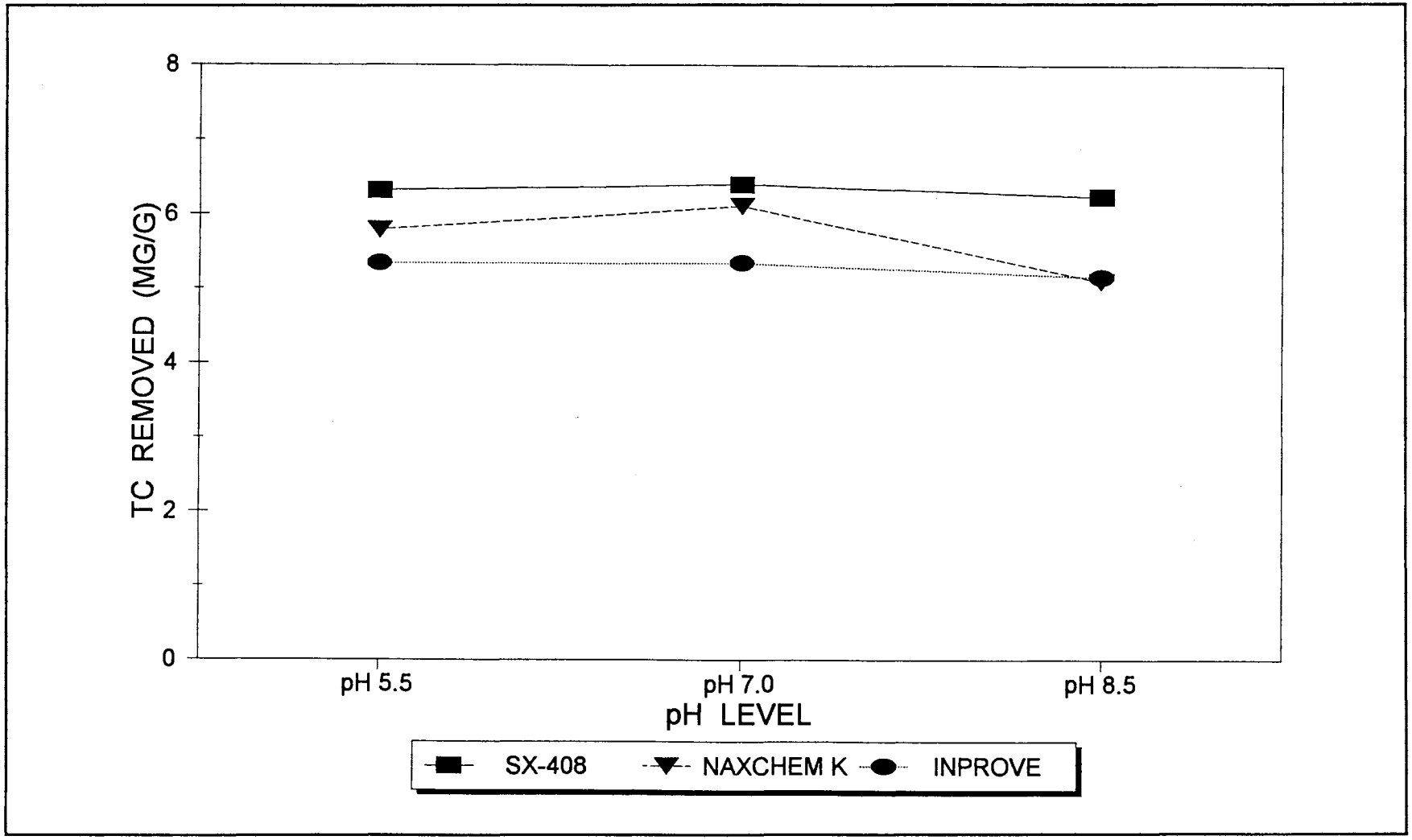

Figure 21. Average Amount of All Target Compounds Removed by the Surfactants SX-408, NAXCHEM K, and INPROVE at Each pH Level (Hypothesis 6, Table 33)

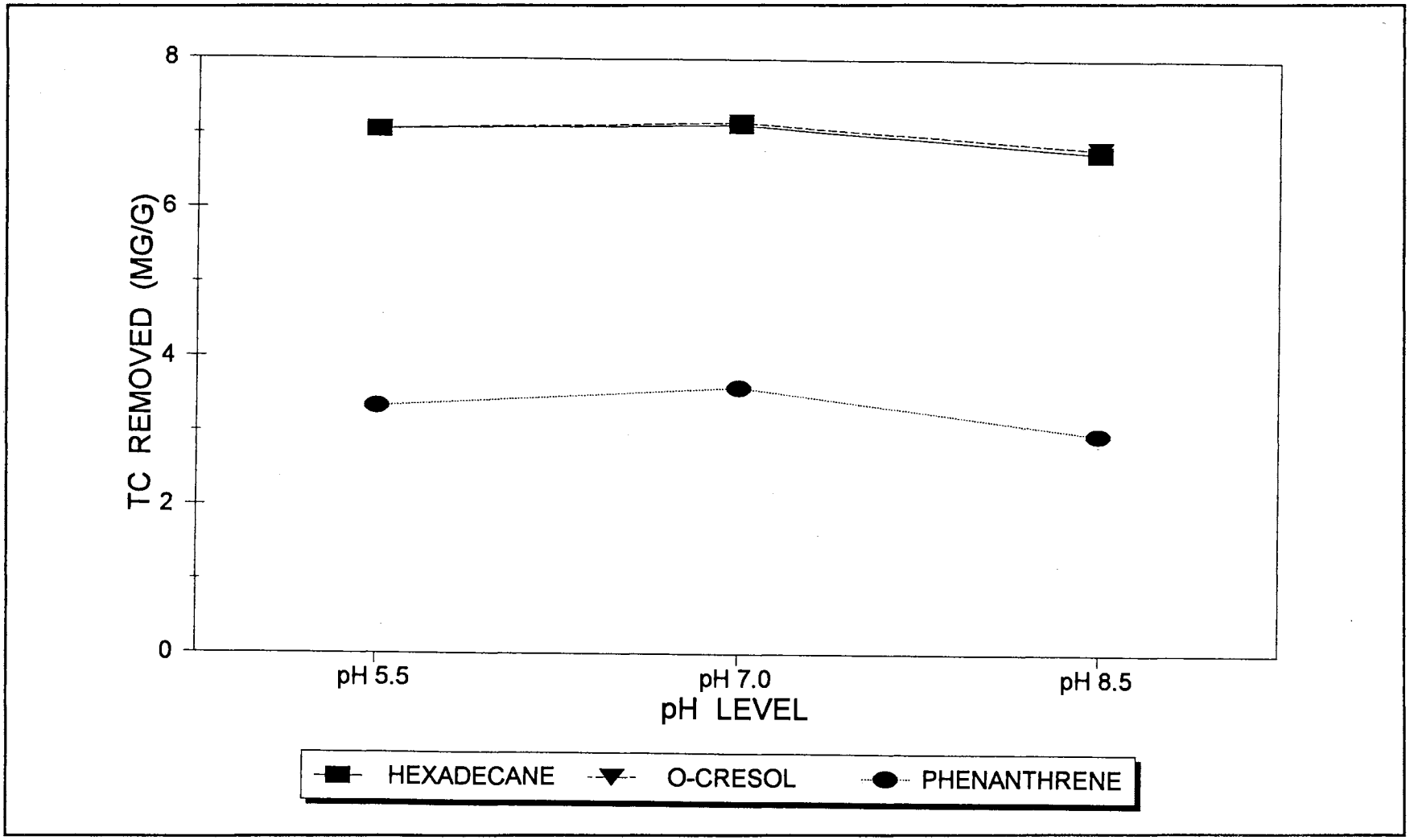

Figure 22. Average Amount of the Target Compounds Hexadecane, O-Cresol and Phenenthrene Removed at Each pH Level (Hypothesis 6, Table 34)

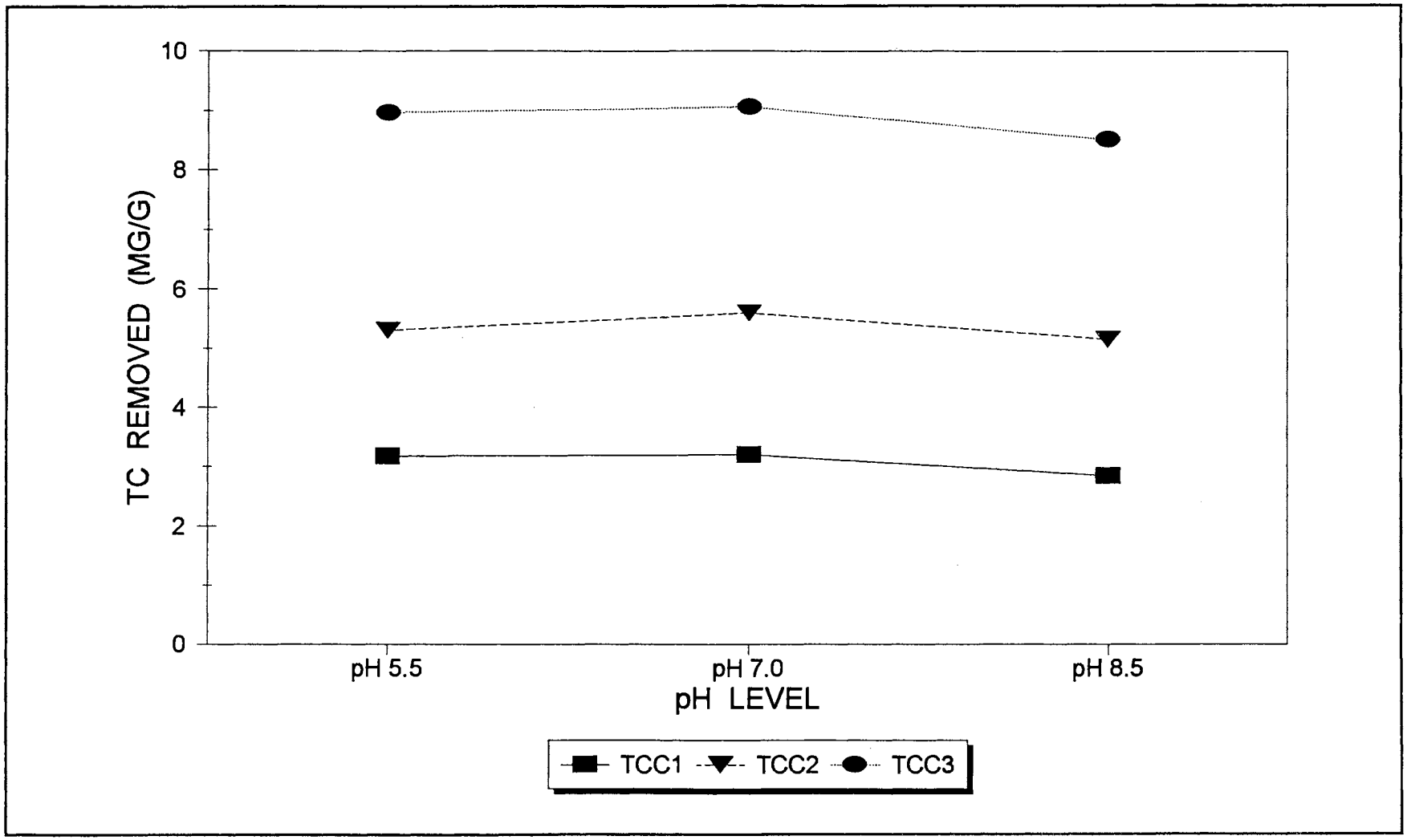

Figure 23. Average Amount of All Target Compounds Removed for Each Target Compound Concentration at Each pH Level (Hypothesis 6, Table 35)

TARGET COMPOUND * BRINE, and TARGET COMPOUND CONCENTRATION * BRINE interactions indicate that the differences were not statistically different (Table 24 and 36). Therefore, the hypothesis was not rejected.

Although the means were not statistically significant, they have been plotted. The nonsignificance of the mean differences for the tested variable is indicated by the flat lines in the graphs. The SURFACTANT * BRINE interaction means from Table 37 were plotted in Figure 24. Figure 25 displays the plotted TARGET COMPOUND * BRINE interaction means (Table 38). These plotted data appear quite similar to Figure 22: the target compound solubilities are reflected in the location of the straight lines for each target compound. The hexadecane (TC1) and o-cresol (TC2) were statistically different from phenanthrene (TC3) but for all brine levels there were no differences. The plotted means from Table 39 represent the means for the TARGET COMPOUND CONCENTRATION * BRINE interactions (Figure 26). Here the distinct differences in the target compound concentration means appear quite similar to the TARGET COMPOUND CONTRATION * pH interactions (Figure 23). While each target compound concentration is not significant over the brine range, they are significantly different from each other.

Hypothesis 8

Hypothesis 8, in the null form, stated that there are no differences between types (T) of flushes, surfactant flushes (T1) and water alone flushes (T2), in terms of the mg of target compound desorbed from the soil with respect to target compounds, or levels of target compound concentration, brine or pH. The ANOVA data for the

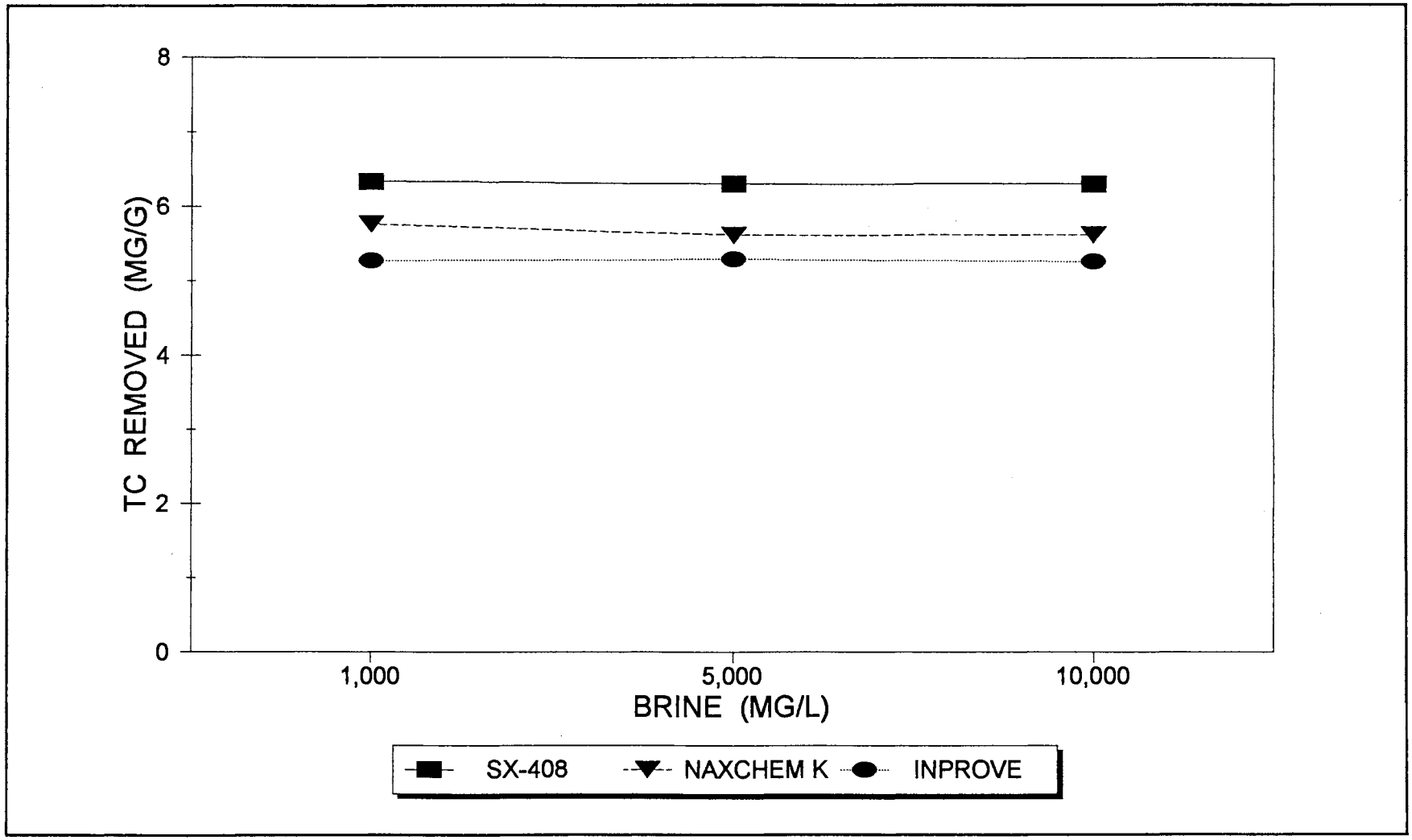

Figure 24. Average Amount of All Target Compounds Removed by the Surfactants SX-408, NAXCHEM K and INPROVE for Each Brine Concentration (Hypothesis 7, Table 37)

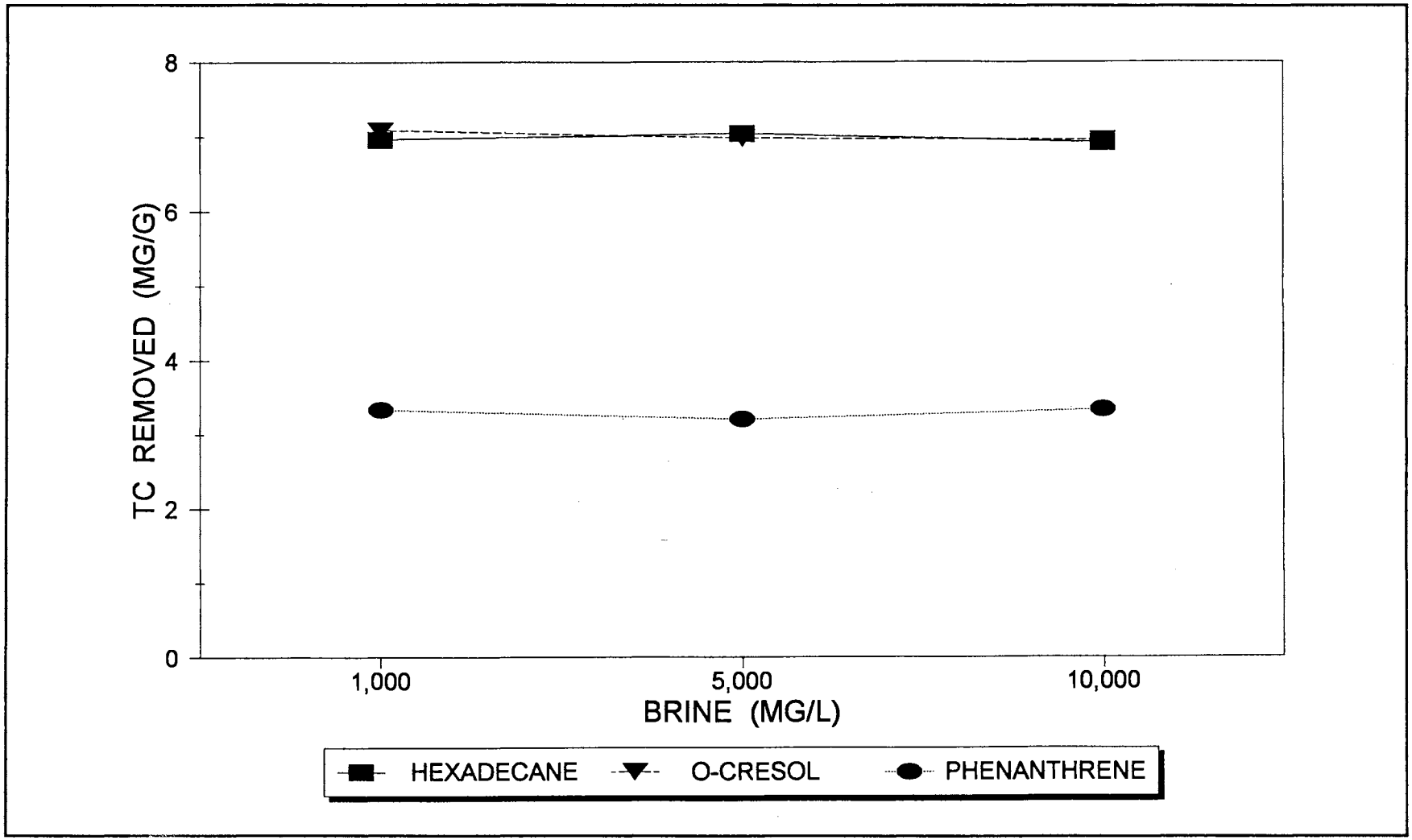

Figure 25. Average Amount of the Target Compounds Hexadecane, O-Cresol and Phenenthrene Removed at Each Brine Concentration (Hypothesis 7, Table 38)

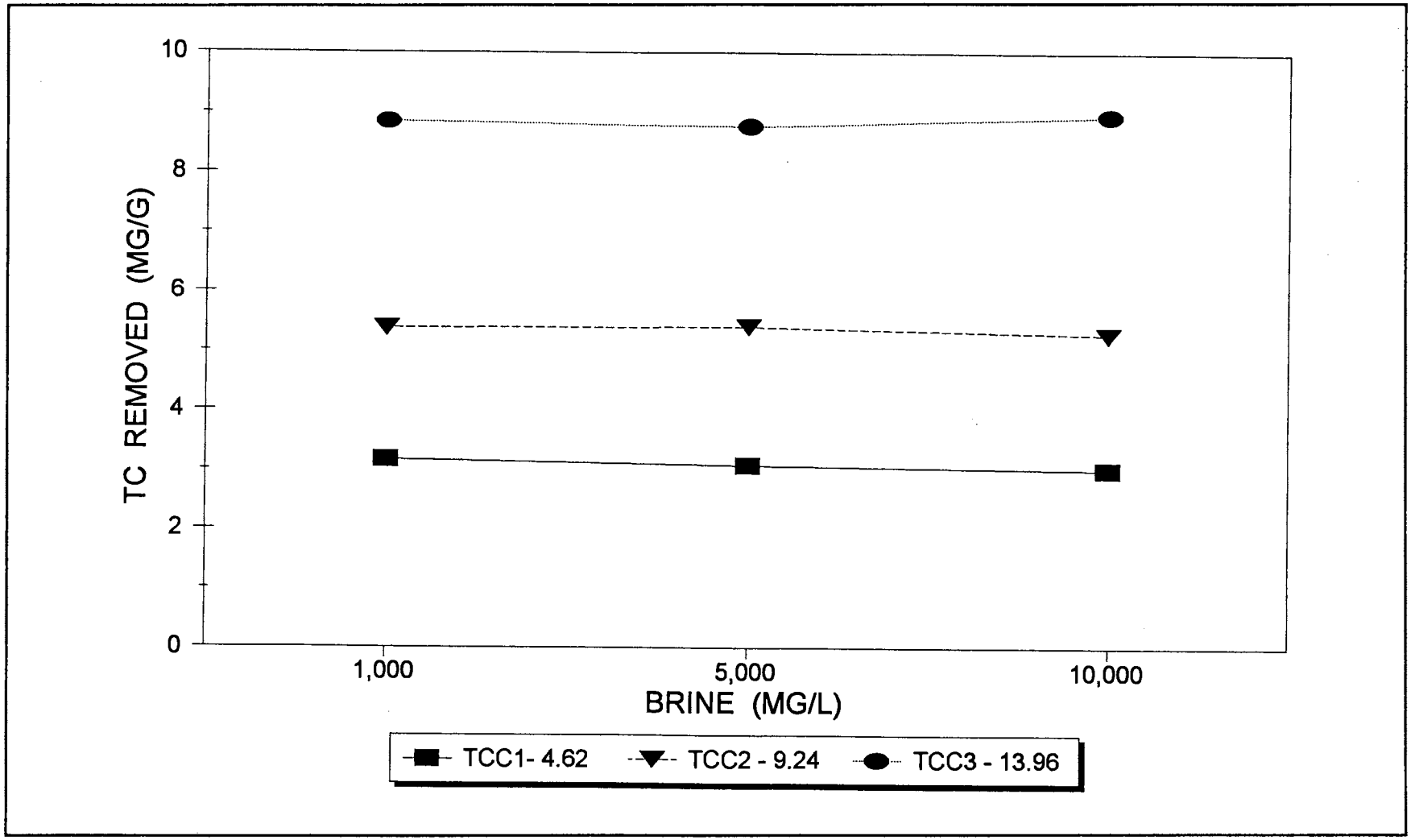

Figure 26. Average Amount of All Target Compounds Removed at Each Target Compound Concentration and Brine Concentration (Hypothesis 7, Table 39)

interactions testing this hypotheses indicated that for the following variables there was a significant difference between the surfactant flush and the water flush: TYPE, TARGET COMPOUND, TARGET COMPOUND CONCENTRATION, TYPE * TARGET COMPOUND, TYPE * TARGET COMPOUND CONCENTRATION, TARGET COMPOUND * TARGET COMPOUND CONCENTRATION and TYPE * TARGET COMPOUND * TARGET COMPOUND CONCENTRATION (Table 40). For the variables BRINE, pH, and their various interactions, however, there were no significant differences. Therefore, within the levels tested, these variables (BRINE and pH) should not impact an ISSSF remediation system.

The first analysis for TYPE shows that surfactant solutions remove more target compound than do water flushes for hexadecane and phenanthrene. But for o-cresol, the water flush removed an amount equivalent to the surfactant flush (Table 19 and Figure 27). The Tukey test data for the target compounds indicate no significant difference between the following 3 pairs: o-cresol water and surfactant flushes, the hexadecane and o-cresol surfactant flushes, and the o-cresol water flushes and hexadecane surfactant flushes (Table 41).

Figure 28 presents the data for the target compound concentration means from Table 19. The Tukey test data for those interactions indicates only two pairwise means were not significant: surfactant flush for target compound concentration 1 (TCC1) with water flush for target compound concentration 2 (TCC2) and surfactant flush for target compound concentration 2 (TCC2) with water flush for target compound concentration 3 (TCC3) (Table 42).

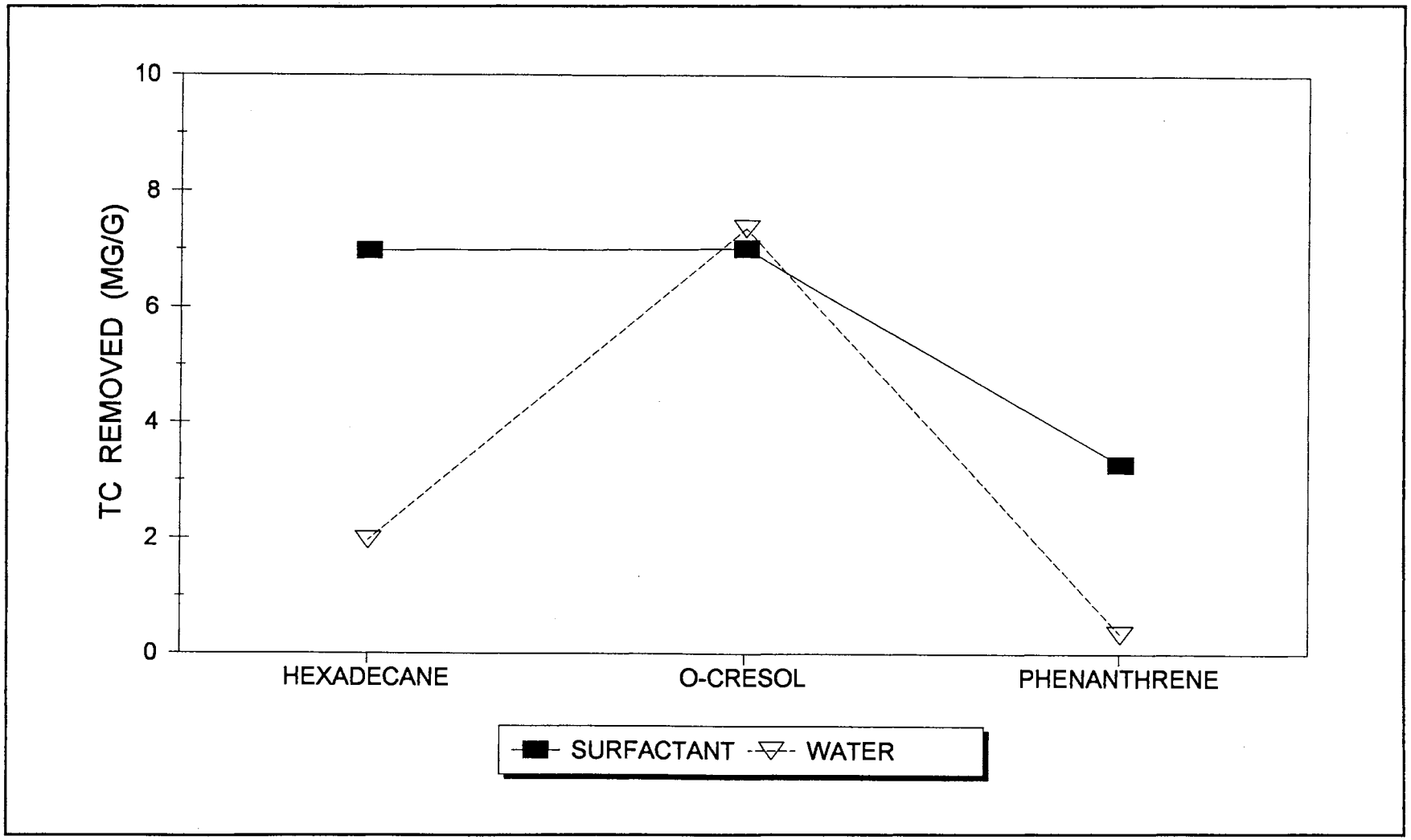

Figure 27. Average Amount of the Target Compounds Removed by All Surfactants and Water Flushes (Hypothesis 8, Table 19)

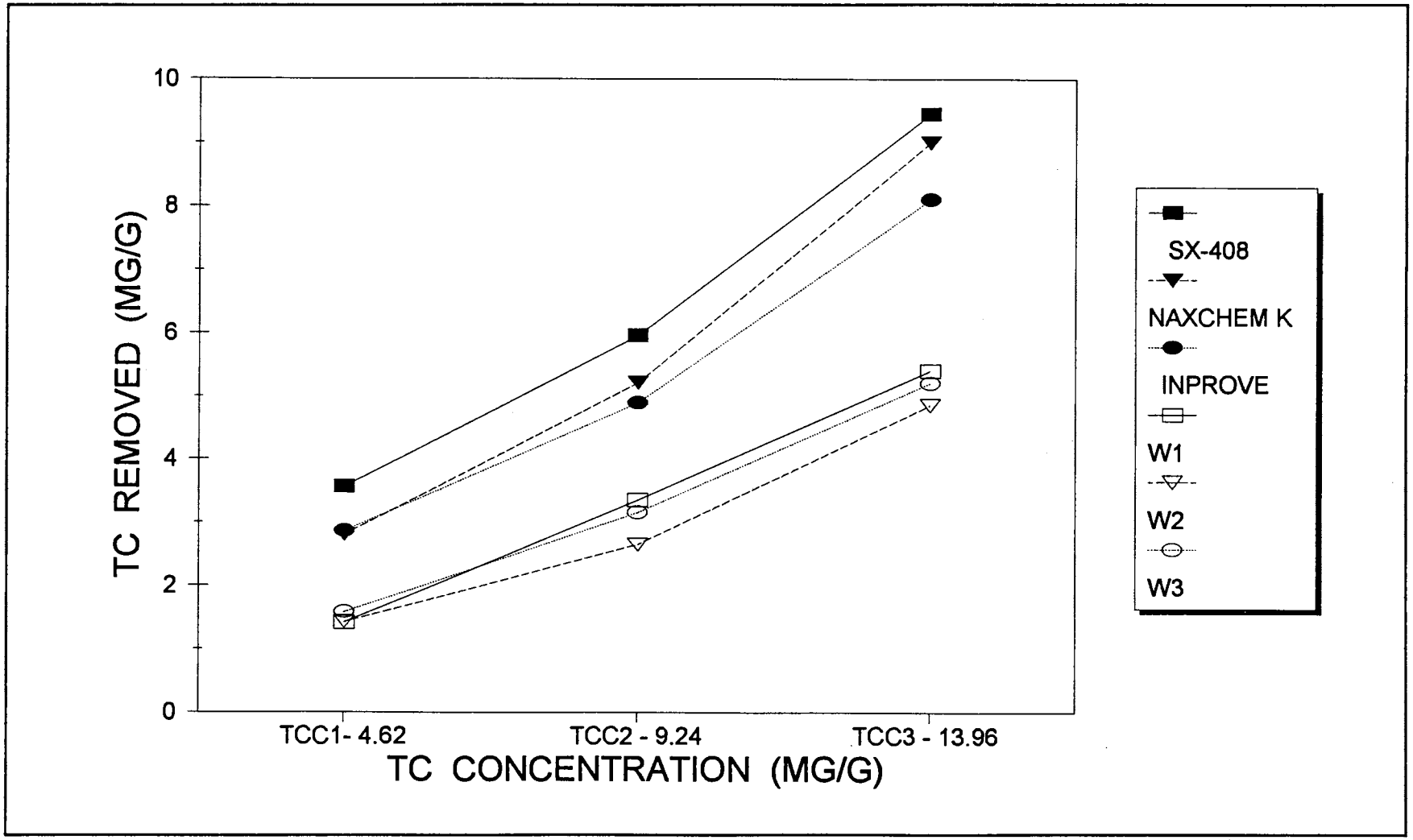

Figure 28. Average Amount of All Target Compounds Removed by All Surfactants and Water Flushes at Each Target Compound Concentration (Hypothesis 8, Table 19)

The first portion of this hypothesis was rejected; there was a difference between surfactant flushes and water flushes for target compounds and target compound concentrations. The later portion of the hypothesis was not rejected, there were no differences between the amount of target compound desorbed across brine and pH levels for the two types of flushes (Table 43). Although not significant, the brine and pH means from Table 19 are plotted in Figures 29 and 30.

Post Hoc/Subsidiary Analyses

A number of portions of analyses were conducted, in addition to those which have been reported, which related to specific hypotheses. Some of the segments of these analyses were significant and may extend our knowledge of the relationships of the variables examined.

TARGET COMPOUND * SURFACTANT CONCENTRATION Interaction.

The first subsidiary analysis indicates that the TARGET COMPOUND * SURFACTANT CONCENTRATION interactions were significant for the surfactant flushes (Table 21). The interaction means from Table 44 indicate that all the surfactant concentrations performed the same for the removal of o-cresol (Figure 31). Greater differences were observed for hexadecane. Phenenthrene appeared from the graph to have the largest differences with the three surfactant concentrations. Tukey test data indicate other pairwise differences were statistically significant overall (Table 45).

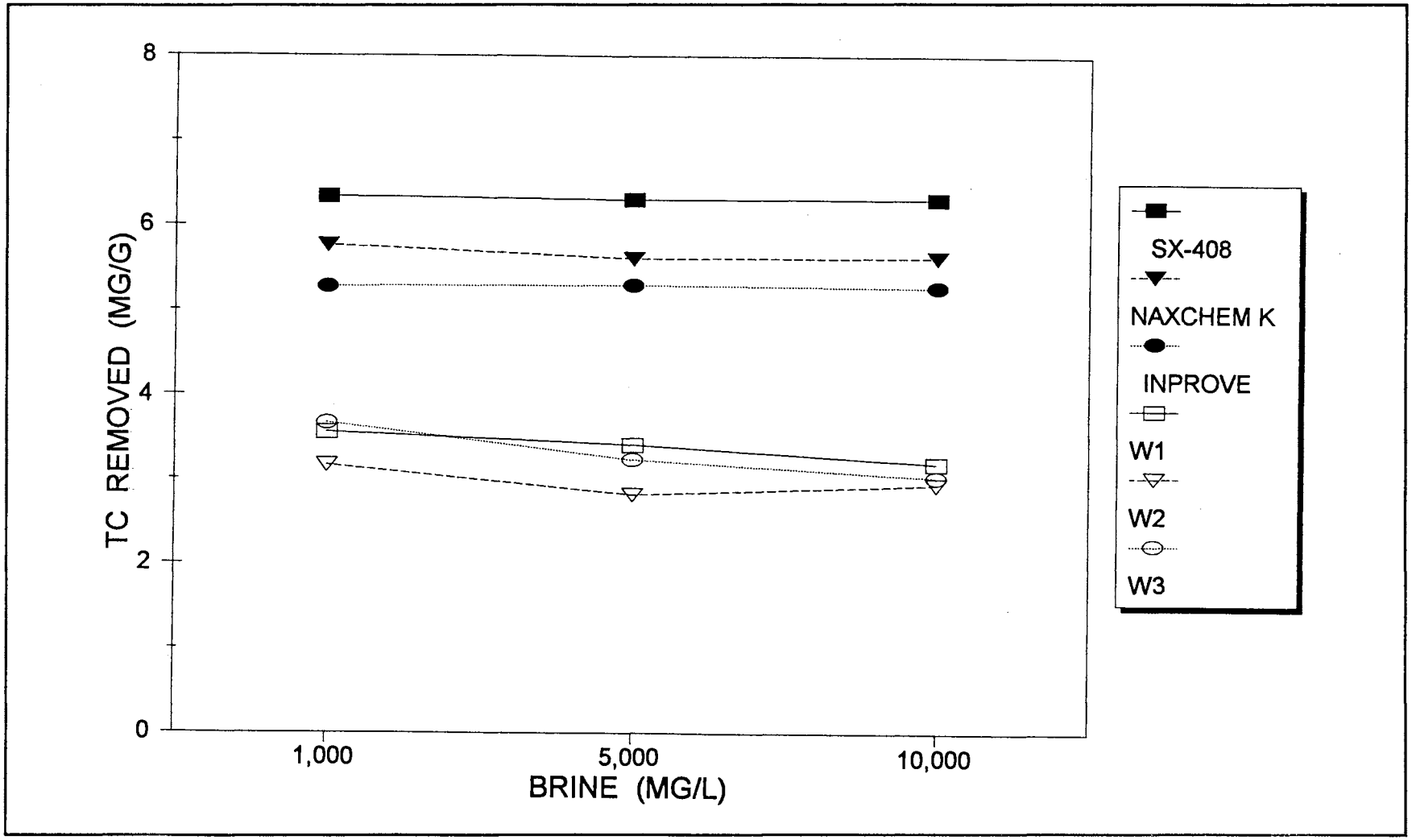

Figure 29. Average Amount of All Target Compounds Removed by All Surfactant and Water Flushes at Each Brine Concentration (Hypothesis 8, Table 19)

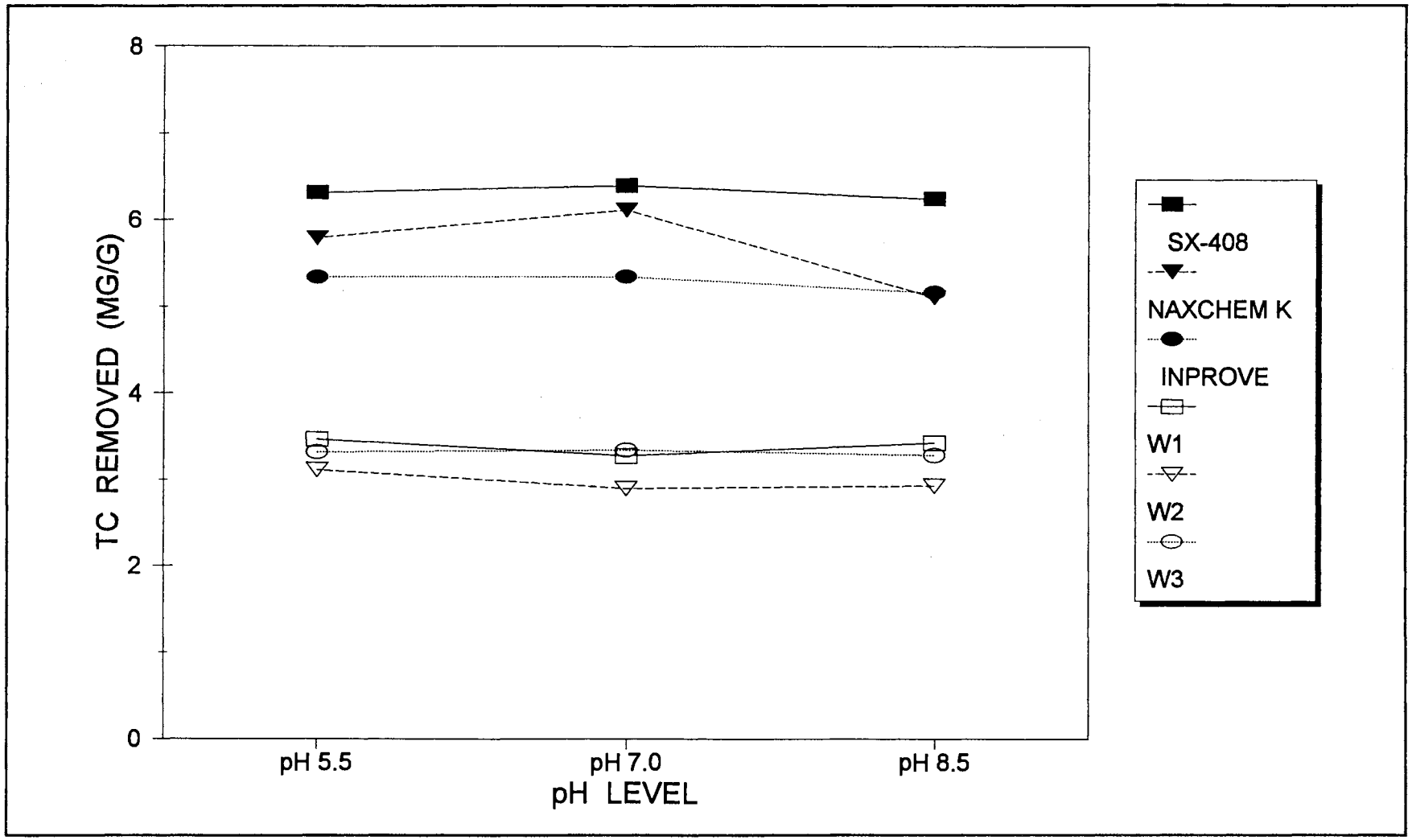

Figure 30. Average Amount of All Target Compounds Removed by All Surfactants and Water Flushes at Each pH Level (Hypothesis 8, Table 19)

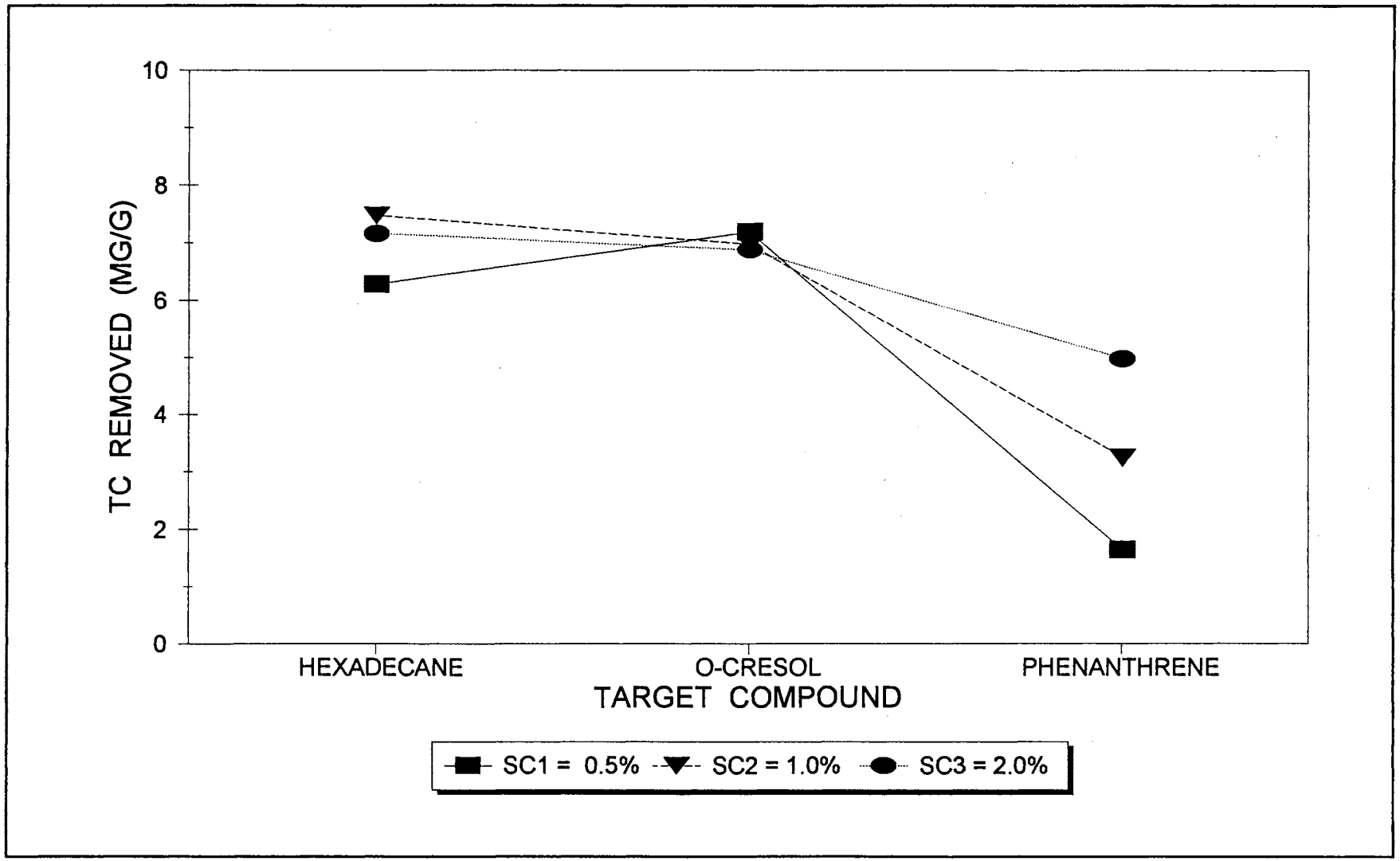

Figure 31. Average Amount of Each Target Compound Removed at Each Surfactant Concentration (Table 44)

SURFACTANT * TARGET COMPOUND * TARGET COMPOUND CONCENTRATION Interaction. Another undiscussed significant interaction was the three-way interaction of SURFACTANT * TARGET COMPOUND * TARGET COMPOUND CONCENTRATION for surfactant flushes (Table 22). The corresponding means from Table 46 are plotted separately for each surfactant (Figures 32-34).

The sums from Table 46 show that S1 (SX-408) removed a total of 23.97 mg/g of hexadecane (TC1), 18.58 mg/g of o-cresol (TC2) and 14,34 mg/g of phenanthrene (TC3). For S1 (SX-408), there was little difference in the removal of all the target compounds at target compound concentration 1 (TCC1) (Figure 32). At target compound concentrations 2 and 3 (TCC2 and TCC3), the order of target compound removal for SX-408 was hexadecane, o-cresol and phenanthrene (TC1, TC2 and TC3). SX-408 (S1) removed more hexadecane (TC1) at all target compound concentrations (23.97 mg/g) than did NAXCHEM K or InProve (S2 or S3).

S2 (NAXCHEM K) removed 17.91 mg/g of hexadecane, 21.10 mg/g o-cresol and 12.04 mg/g of phenanthrene. For S2 (NAXCHEM K), the order of target compound removal was o-cresol, hexadecane and phenanthrene with data similar to that of S1 data for all target compounds at target compound concentration 1 (TCC1) (Figure 33). The hexadecane (TC1) and o-cresol (TC2) data plot nearly parallel lines.

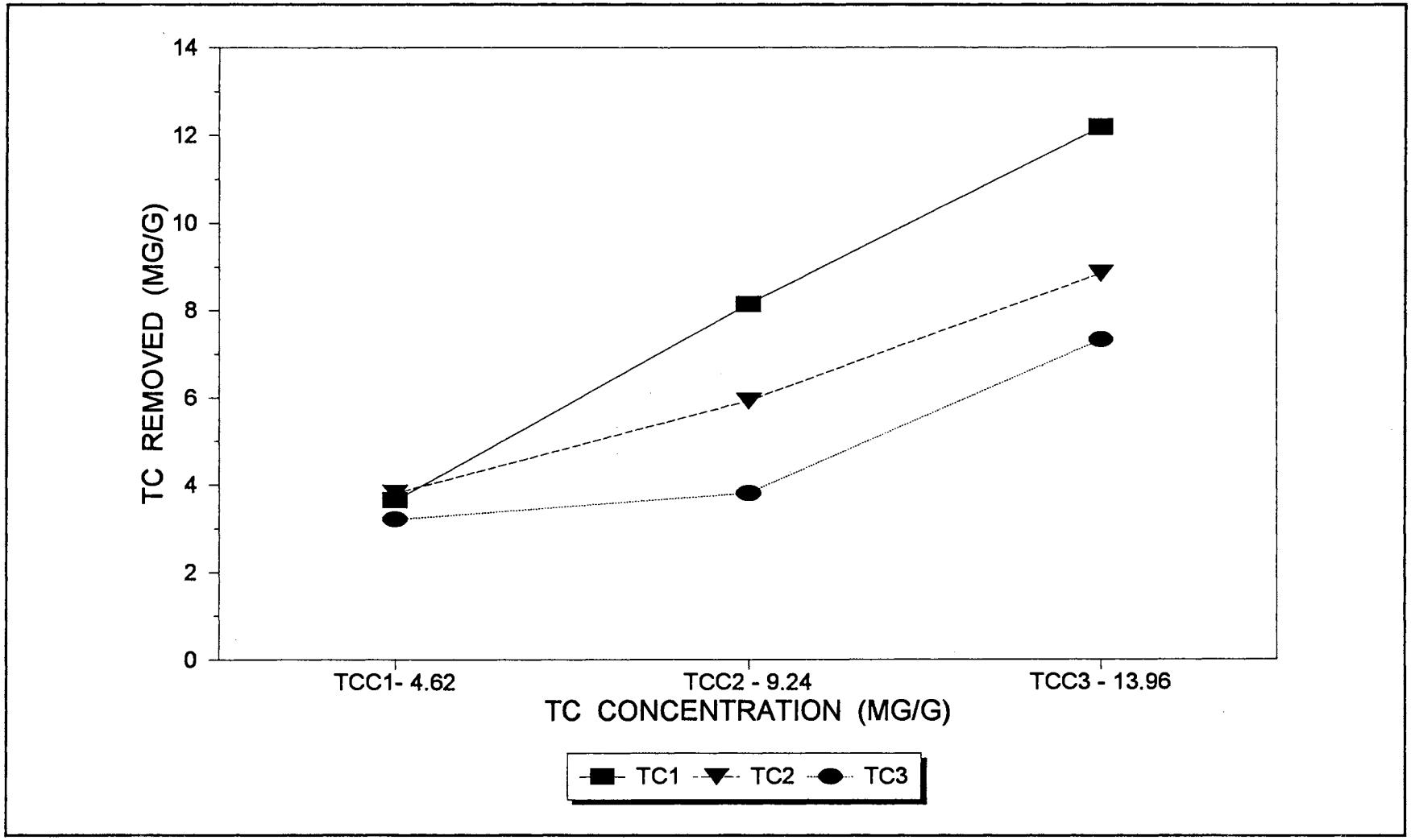

Figure 32. Average Amount of Each Target Compound (TC1 = Hexadecane, TC2 = O-Cresol and TC3 = Phenanthrene) Removed at Each Target Compound Concentration with SX-408 Surfactant (S1) (Table 46)

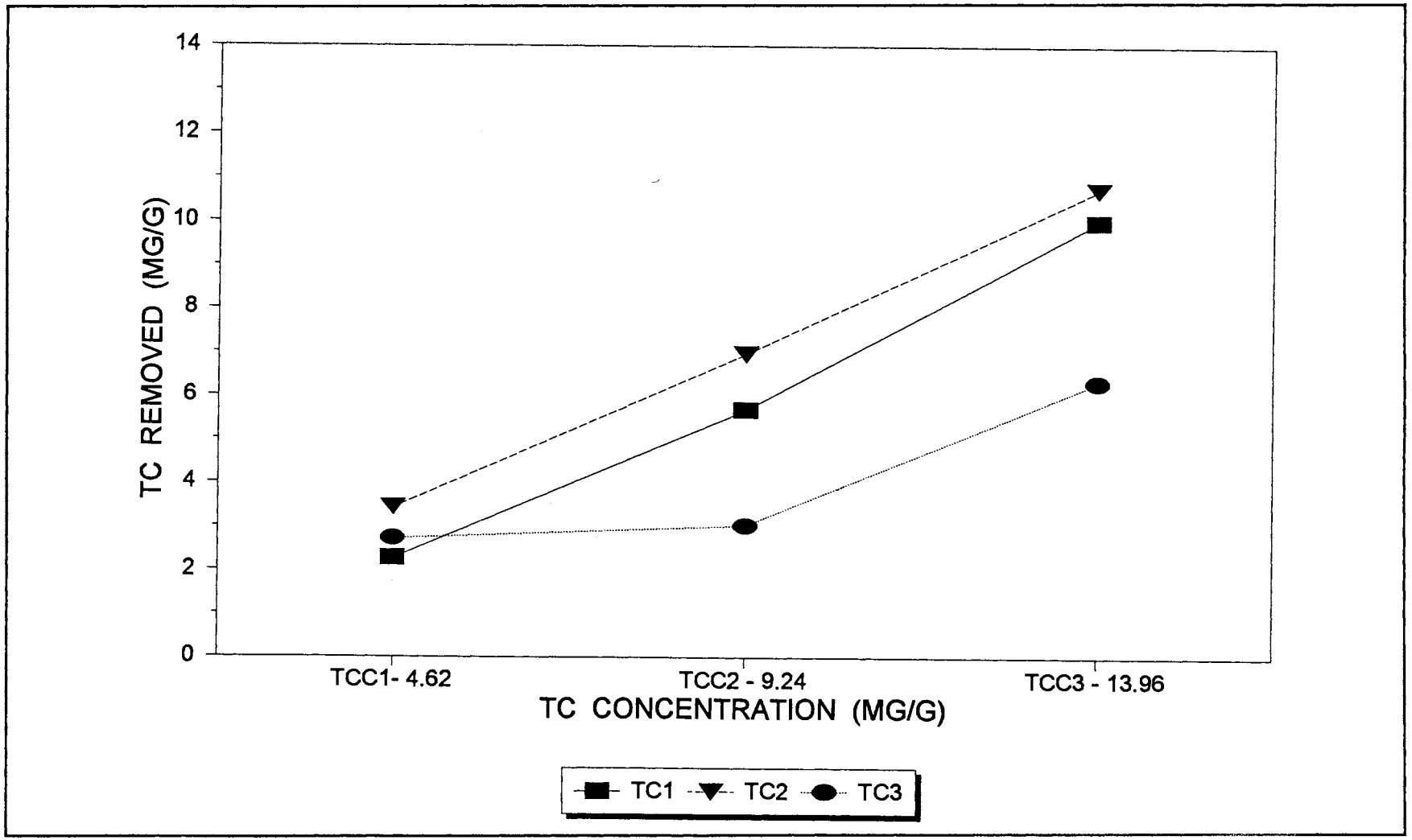

Figure 33. Average Amount of Each Target Compound (TC1 = Hexadecane, TC2 = O-Cresol and TC3 = Phenanthrene) Removed at Each Target Compound Concentration with NAXCHEM K Surfactant (S2) (Table 46)

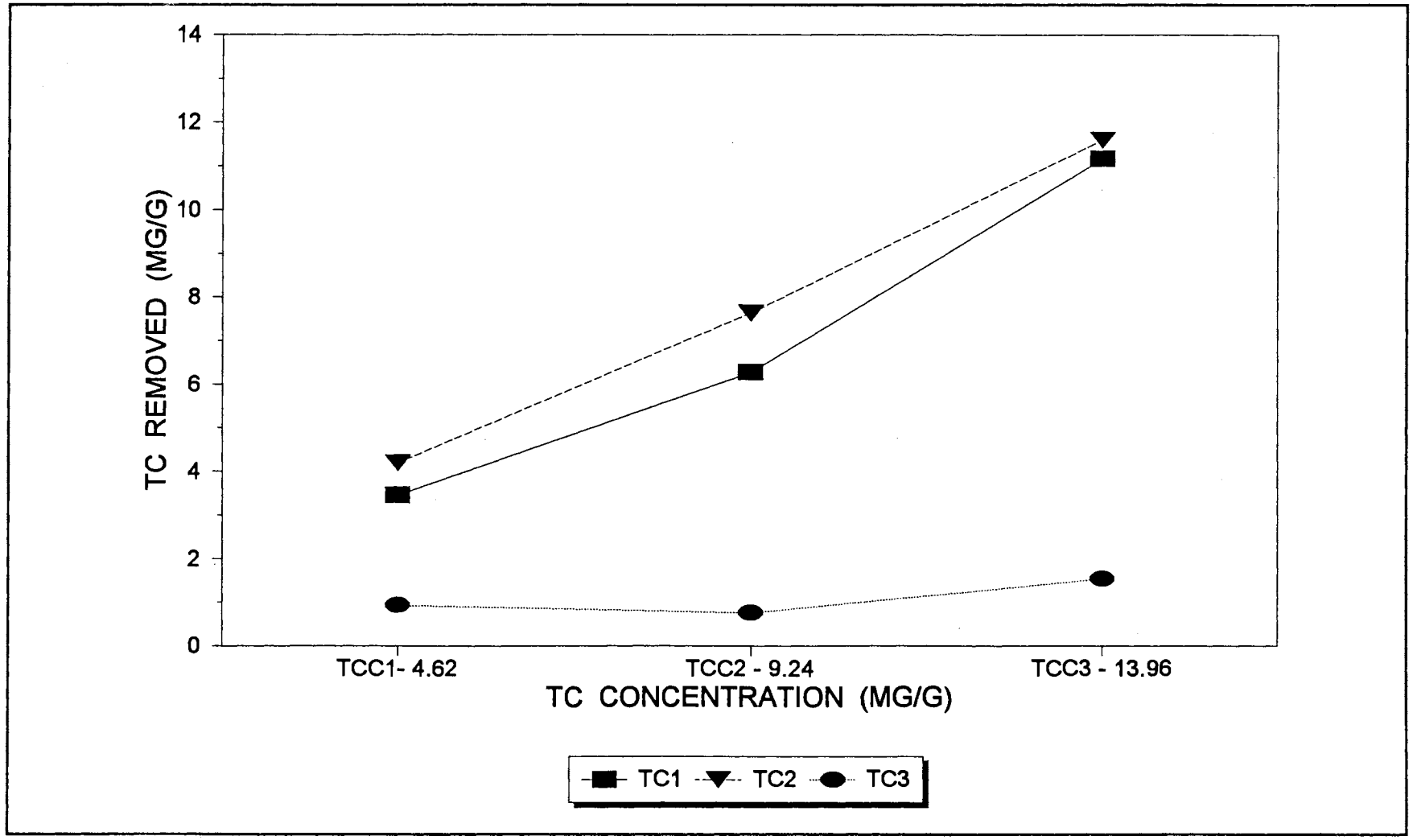

Figure 34. Average Amount of Each Target Compound (TC1 = Hexadecane, TC2 = O-Cresol and TC3 = Phenanthrene) Removed at Each Target Compound Concentration with INPROVE Surfactant (S3) (Table 46)

S3 (InProve) was the least effective surfactant in removing the phenanthrene (3.23 mg/g) (Figure 34). However, S3 removed more o-cresol (23.42 mg/g) than did S2 or S1.

At target compound concentration 1 (TCC1), 68% of the hexadecane (TC1), 99% of the o-cresol (TC2) and 50% of the phenanthrene (TC3) was removed. At TCC2, 72% of hexadecane, 61% of o-cresol and 27% of phenanthrene was recovered. At target compound concentration 3 (TCC3), 80% of the hexadecane, 74% of the o-cresol and 36% of the phenanthrene was recovered. Tukey test data are presented in Tables 47 and 48.

TYPE * TARGET COMPOUND * TARGET COMPOUND CONCENTRATION Interaction. In the three-way ANOVA (Table 40) of this interaction, the T (T = type of flush, i.e., water wash or surfactant) analysis was significant. The means (Table 49), Tukey test data (Tables 50 and 51) and the plotted means (Figure 35) indicated that for hexadecane and phenanthrene, the surfactant flushes had higher amounts of target compound desorbed than the water flushes. For o-cresol, however, the water flushes removed more target compound than the surfactant flush. However, the apparent difference of the two flushes for o-cresol was not a significant difference. For hexadecane (TC1) the total mg/g desorbed was 20.93 for the surfactant flushes and 5.88 for the water flushes. For o-cresol (TC2) the total mg/g desorbed was 21.03 for the surfactant flushes and 22.09 for the water flushes. For phenanthrene (TC3) the total mg/g desorbed was 9.87 for the surfactant flushes and 1.04 for the water flushes.

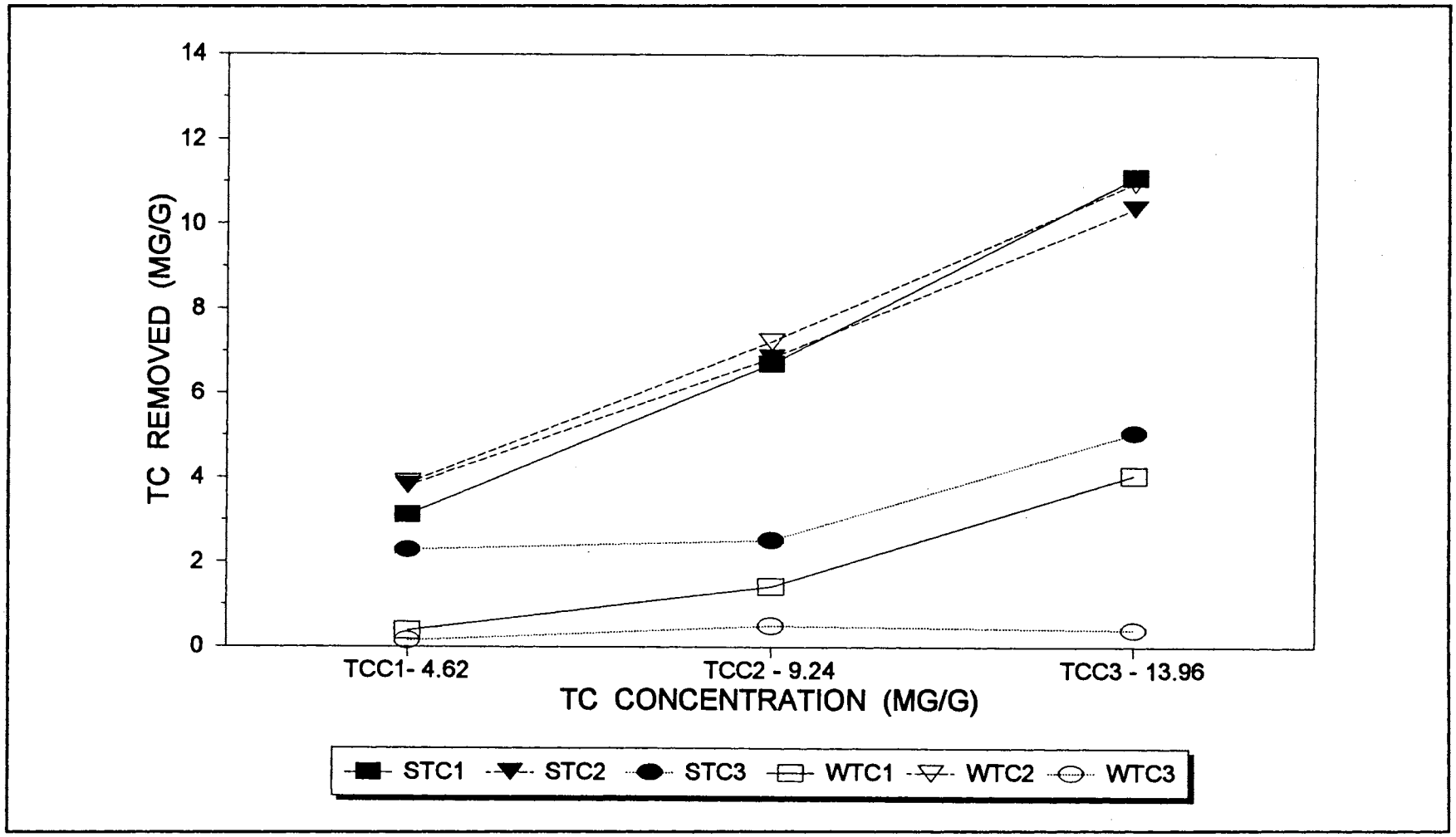

Figure 35. Average Amount of Each Target Compound (TC1 = Hexadecane, TC2 = O-Cresol and TC3 = Phenanthrene) Removed at Each Target Compound Concentration with Surfactant Flushes (S) and Water Flushes (W)(Tab.49)

For hexadecane (TC1), the differences between the surfactant and water flushes were significant at all three target compound concentrations. At target compound concentration 1 (TCC1), the surfactant flushes removed 2.738 mg/g more hexadecane than the water flushes. At target compound concentration 2 (TCC2), the surfactant flushes removed 5.259 mg/g more hexadecane than the water flushes. At target compound concentration 3 (TCC3), the surfactant flushes removed 7.051 mg/g more hexadecane than the water flushes.

For o-cresol (TC2), there were no significant differences in the surfactant flushes and the water flushes at any of the target compound concentrations. Also, there were no differences between the hexadecane surfactant flushes and any of the o-cresol flushes.

For phenanthrene (TC3), the differences between the surfactant flushes and the water flushes at all target compound concentrations were significant. The water flushes removed < 0.5 mg/g phenanthrene at each of the three surfactants. At target compound concentration 1 (TCC1), the surfactant flush removed 2.145 mg/g more phenanthrene than the water flushes. At target compound concentration 2 (TCC2), the surfactant flushes removed 2.028 mg/g more phenanthrene than the water flushes. At target compound concentration 3 (TCC3), the surfactant flushes removed 4.662 mg/g more phenanthrene than the water flushes.

There was no difference between the water flush of hexadecane (TC1) and phenanthrene (TC3) at target compound concentration 1 (TCC1). At target compound concentration 2 and 3 (TCC2 and TCC3), however, the differences were significant.

In this same analysis there was an significant main effect for flush type (T)

(Table 40) comparing surfactant to water wash flushes. Combining the target compounds, the surfactant flushes (17.27 mg/g) were clearly more effective in removing the target compound contaminant than were the water flushes (9.67mg/g).

Blanks. Two other subsidiary analyses deserve consideration and explanation; the sample blanks and replicate samples analyses. One blank was prepared for each sample (729 total). The blanks were examined descriptively. The blank means ranged from 0.085 mg/g to 0.556 mg/g with an average of 0.223 mg/g. The means for the various target compounds and surfactant blanks (Table 52) are tightly grouped for all levels of both variables indicating little sampling bias. The blanks were not, therefore, subtracted from the samples.

Replicates. Three replicates of each sample (2187 total) were prepared as part of the QA/QC procedures. The replicates were statistically tested by a one-way ANOVA to determine if any systematic bias had been introduced. The ANOVA data (Table 53) indicate no significant differences. Thus the replicates could be averaged with no consequent experimental bias. To dampen any effects of experimental error, the replicates were averaged for each sample before the data analyses.

CHAPTER V

CONCLUSIONS

Of the 8 hypotheses tested in this study, 6 were rejected and 2 were not rejected. The hypotheses that concerned the main effect and some interactions of the variables solution type, surfactant, surfactant concentration, target compound and target compound concentration were rejected as these variables significantly influenced the desorption of the target compounds from the soil. The hypotheses that concerned brine and pH, as main effects and in interactions with other variables, were not rejected as the two variables did not significantly influence the desorption of the target compounds from the contaminated soil. Statistical analyses included a maximum of three variables. Synergistic effects of all variables were not tested and are, therefore, difficult to predict.

Surfactant solution flushes desorbed target compounds that are normally insoluble in water and were not desorbed in water type flushes alone. Pump-and-treat systems for the remediation of immiscible (hydrophobic) contaminants can be enhanced with surfactant solutions to increase the amount of contaminant flushed from the soil and reduce the life-cycle time frame of the system.

The surfactants' effectiveness differed for the overall target compound removal as well as for the individual target compound removal. Overall, Sandoxylate SX-480 (S1) was the most effective surfactant and InProve (S3) was the least effective in

desorbing all the target compounds. The differences between SX-408 and NAXCHEM K and the differences between NAXCHEM K and InProve were not significant. Individually, SX-408 was most effective for removing hexadecane and phenanthrene while InProve was most effecitive in removing o-cresol. NAXCHEM-K was least effective in removing hexadecane. These data imply that there is not any one universal surfactant that equally desorbs all target compounds as the surfactants were differentially effective for various target compounds.

The surfactant solution concentration directly influenced the amount of contaminant removed. Overall, the 2% surfactant solution removed more TC than the 0.5% solution. However, there was no statistical difference between 0.5% and 1.0% as well as no difference between 1.0% and 2.0%. Individually, the SX-408 surfactant removed more TC at 2 surfactant solution concentrations than NAXCHEM K or InProve. At the lowest concentration (0.5%), the three surfactants desorbed the same amount of contaminants when all the target compounds were taken as a group. As the surfactant concentration increased, the differences in the amount of contaminants desorbed by the individual surfactants became more pronounced with SX-408 desorbing the most and InProve desorbing the least at 1.0% and 2.0%. Each surfactant has an optimum effective concentration at which point increases in surfactant concentration do not result in further increases in desorption of the target compound.

Not all target compounds desorb to the same extent with surfactant flushing. Three target compounds were used in this study: hexadecane. o-cresol and

phenanthrene. The 3 chosen compounds represent 3 groups of hydrocarbons found at contaminated sites: aliphatic, alkyl-aromatic and polynuclear aromatic hydrocarbons, respectively. These 3 target compounds were expected to desorb differently due to their chemical/physical characteristics and did so. With the surfactants used in this study, greater amounts of hexadecane and o-cresol were desorbed than phenanthrene. Applying the data to the represented compound groups indicate that greater amounts of aliphatics and alkyl-aromatics desorb than polynuclear aromatics. For the individual surfactants, the SX-408 surfactant would be expected to be most effective with aliphatics and polynuclear aromatics and the InProve surfactant to be most effective with alkyl-aromatic compounds

Target compound concentration on the soil affected the amount of contaminant desorbed by each surfactant. At the levels tested, each surfactant desorbed more target compound at the corresponding higher target compound concentrations. These data indicated that the surfactant-enhanced solubility limit of the contaminants was not reached. The greater the concentration of the target compound in the soil, the greater the mass of target compound desorbed. This finding supported the theory of Sale and Pitts, 1989, that the first flush would produce the greatest contaminant removal and has the greatest economic impact in terms of surfactant used, recovered effluent treatment, and life cycle design of the system parameters. Multiple flushes at a site would address the problem of exceeding the surfactant-enhanced solubility of the contaminants as well as temporal and spatial variability of contaminants.

Brine or pH did not influence desorption of target compounds for all surfactant and water flushes with the experimental variables of this study. The brine level of the solution which flushed the soil does not make a difference in terms of the amount of the target compounds desorbed when related to surfactant type, surfactant concentration, target compound type and target compound concentration. This finding supported the transfer of the technology from the surfactants' use as oil dispersants in marine spills to flushing hydrocarbon contaminated soils with freshwater, brackish or saline ground water quality. The pH level of the flushing solution did not interact with the surfactant type, the surfactant concentrations, the target compound type and the target compound concentrations. This finding confirmed the applicability of the tested surfactants to varying ground water pH conditions.

This study supports the technology transfer of enhanced oil recovery to *in situ* remediation of hydrocarbon contaminated soils. The results of this study substantiate the claim that pump-and-treat systems alone are not a viable method of remediating hydrophobic contaminated soils. Surfactant flushing is a viable enhancement of pump-and-treat remediation systems for hydrophobic hydrocarbons.

CHAPTER VI

RECOMMENDATIONS FOR FUTURE STUDIES

As hazardous waste sites continue to be added to the National Priority List, unfavorable economic considerations of long term remediation costs, and the public impatience with the present remediation speed, demand more rapid and successful remediation of the sites. *In situ* surfactant-enhanced soil flushing is a remediation technique which, when applicable, may address these demands. Further research is recommended to more precisely define the influence and/or the uncertainty of the variables involved in ISSSF and the applicability of the system.

* Testing the effectiveness of the system with various types of water hardness would extend the applicable range of the system and define site-specific effectiveness.
* Temperature has a great effect on the surface tension of NAPLS : the influences of temperature on the system would delineate seasonal influences on desorption rates as well as more closely simulate subsurface environments.
* Contaminated soil from an actual site would be more realistic in terms of competing effects of contaminant mixtures and synergistic effects.
* Further exploration of the effects of pH with other surfactants and/or target compounds would also assist in delineating the effectiveness of the system with varying ground water quality.

* The method of contamination of the soil could be varied to allow for more contact time between the soil and the target compounds or actual weathered field soil could be used.
* The enhancement of bioremediation by pre or simultaneous surfactant flushing would broaden the applicability of the system.
* Follow-up studies with soil columns would determine the validity of the batch data.
* System models developed from basic research which defined interactions, rates and mechanisms would delineate the applicability of the system.
* Studies with multiple target compound mixtures would test for synergistic effects and interactions.
* Studies of mixtures of surfactants could combine favorable properties of each surfactant to check for mutual enhancement or deleterious interactive effects.
* Additional soil types could check for applicability to different site characteristics.
* Studies with variable soil water content (ranging from unsaturated to saturated) would test the system efficiency will delineate optimal conditions and define expected desorption rates under varying conditions.
* Soil column studies with a series of water and surfactant solution flushes would optimize the sequence of flushes to minimize expense.
* Economic analyses of the above studies to delineate economic considerations within the system and for comparison with other remedial systems.

* Investigation of the effect of surfactant solution contact time on the effectiveness of desorption in soil columns.
* Further delineation of the influence hydraulic conductivity could assist in relating the system usage to wider range of hydrogeologic conditions.
* Define quantitative structure activity relationships (QSAR) of the variables.
* Economic comparisons of one flush with high concentration of surfactant compound versus several flushes with lower concentrations could be determined from the effectiveness of the respective flushes.
* Toxicity test of the selected or other oil dispersant surfactants would delineated their environmental impact.

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APPENDIX

TABLE 18

SUMMARY OF MAIN EFFECTS TESTS (HYPOTHESIS 1)

Main Effect	Level	Symbol	Name or Value	* H°	Significant ?
Surfactant	1	S1	Sandoxylate SX-408	R	Yes
	2	S2	NAXCHEM K		
	3	S3	InProve		
Surfactant	1	SC1	0.5%	R	Yes
Concentration	2	SC2	1.0%		
	3	SC3	2.0%		
Target	1	TC1	Hexadecane	R	Yes
Compound	2	TC2	O-Cresol		
	3	TC3	Phenanthrene		
Target	1	TCC1	4.620 mg/g soil	R	Yes
Compound	2	TCC2	9.240 mg/g soil		
Concentration	3	TCC3	13.860 mg/g soil		
pH	1	pH1	5.5	NR	No
	2	pH2	7.0		
	3	pH3	8.5		
Brine	1	B1	1,000 mg/l	NR	No
	2	B2	5,000 mg/l		
	3	B3	10,000 mg/l		

* R = Rejected NR = Not Rejected H° = Null Hypothesis

TABLE 19

VARIABLE MEANS AND STANDARD DEVIATIONS FOR WATER AND SURFACTANT SOLUTION FLUSHES (HYPOTHESIS 1)

	Surfactant Flushes (T1)		Water Flushes (T2)	
Variable	Mean*	SD*	Mean*	SD*
S1	6.322	3.439	3.384	3.618
S2	5.672	3.689	2.976	3.726
S3	5.283	3.993	3.309	3.818
SC1	5.037	3.511	3.176	3.724
SC2	5.901	3.623	3.219	3.696
SC3	6.339	3.572	3.274	3.758
TC1	6.976	3.939	1.960	2.198
TC2	7.011	2.952	7.363	3.028
TC3	3.291	2.923	0.346	0.724
TCC1	3.076	1.183	1.470	1.726
TCC2	5.351	1.726	3.052	3.164
TCC3	8.851	3.810	5.147	4.672
pH1	5.818	3.581	3.294	3.768
pH2	5.954	3.710	3.168	3.755
pH3	5.506	3.522	3.207	3.653
B1	5.797	3.634	3.463	3.722
B2	5.742	3.690	3.154	3.725
B3	5.739	3.603	3.052	3.719

* Units = mg/g

TABLE 20

TUKEY TEST DATA FOR MAIN EFFECTS VARIABLES (HYPOTHESIS 1)

Variable	Pairwise Mean Differences (mg/g)		
	1	2	3
S1 - SX-408	0.000		
S2 - NAXCHEM K	*-0.649	0.000	
S3 - InProve	-1.039	*-0.389	0.000
SC1 - 0.05%	0.000		
SC2 - 1.0%	*0.864	0.000	
SC3 - 2.0%	1.302	*0.438	0.000
TC1 - Hexadecane	0.000		
TC2 - O-Cresol	*0.035	0.000	
TC3 - Phenanthrene	-3.686	-3.720	0.000
TCC1 - 4.62 mg/g	0.000		
TCC2 - 9.24 mg/g	2.274	0.000	
TCC3 - 13.86 mg/g	5.775	3.501	0.000
pH 1 - 5.5	0.000		
pH2 - 7.0	*0.137	0.000	
pH3 - 8.5	*-0.312	*-0.448	0.000
Brine 1 - 1,000 mg/l	0.000		
Brine 2 - 5,000 mg/l	*-0.310	0.000	
Brine 3 - 10,000 mg/l	*-0.412	*-0.102	0.000

* Not Significant at $P < 0.05$

TABLE 21

ANALYSIS OF VARIANCE USING FACTORS OF SURFACTANTS, TARGET COMPOUNDS AND SURFACTANT CONCENTRATIONS (HYPOTHESES 1A, 1B, 1C, 2, AND 5)

Source	SS[1]	df[2]	MS[3]	F[4]	P[5]
S	133.857	2	66.929	8.291	0.000
TC	2221.474	2	1110.737	137.602	0.000
SC	213.396	2	106.698	13.218	0.000
S * TC	755.237	4	188.809	23.390	0.000
S * SC	61.688	4	15.422	1.911	0.107
TC * SC	304.582	4	76.145	9.433	0.000
S * TC * SC	102.906	8	12.863	1.594	0.123
Error	566.624	702	8.072		

[1] SS = Sum of Squares
[2] df = Degrees of Freedom
[3] MS = Mean Squares
[4] F = F Statistic
[5] P = Exact Probability of the F Statistic Being Different from the Hypothesized Population, e.g., Samples are not Drawn from the Same Population

TABLE 22

ANALYSIS OF VARIANCE DATA COMPARING SURFACTANTS, TARGET COMPOUNDS, AND TARGET COMPOUND CONCENTRATIONS (HYPOTHESES 1D, 3 AND 4)

Source	SS	df	MS	F	P
S	1133.857	2	66.929	32.564	0.000
TC	2221.474	2	1110.739	540.429	0.000
TCC	4113.477	2	2056.739	1000.707	0.000
S * TC	755.237	4	188.809	91.865	0.000
S * TCC	19.939	4	4.985	2.425	0.047
TC * TCC	615.114	4	153.778	74.821	0.000
S * TC * TCC	157.854	8	19.732	9.601	0.000
Error	1442.811	702	2.055		

TABLE 23

ANALYSIS OF VARIANCE USING FACTORS OF SURFACTANTS, TARGET COMPOUNDS AND PHS (HYPOTHESES 1E AND 6)

Source	SS	df	MS	F	P
S	133.857	2	66.929	7.474	0.001
TC	2221.474	2	1110.737	124.033	0.000
pH	25.660	2	12.830	1.433	0.239
S * TC	755.237	4	188.809	21.084	0.000
S * pH	20.075	4	5.019	0.560	0.691
TC * pH	2.091	4	0.523	0.058	0.994
S * TC * pH	14.821	8	1.853	0.207	0.990
Error	6286.548	702	8.955		

TABLE 24

ANALYSIS OF VARIANCE USING FACTORS OF SURFACTANTS, TARGET COMPOUNDS AND BRINES (HYPOTHESES 1F AND 7)

Source	SS	df	MS	F	P
S	133.857	2	66.929	7.411	0.001
TC	2221.474	2	1110.737	122.989	0.000
B	0.524	2	0.262	0.989	0.971
S * TC	755.237	4	188.809	20.906	0.000
S * B	0.703	4	0.176	0.019	0.999
TC * B	1.787	4	0.447	0.049	0.995
S * TC * B	6.271	8	0.784	0.087	1.000
Error	6339.911	702	9.031		

TABLE 25

MEANS AND STANDARD DEVIATIONS FOR SURFACTANTS AND TARGET COMPOUNDS (HYPOTHESIS 2)

Variable	Mean	SD
S1TC1	7.991	3.726
S1TC2	6.193	2.173
S1TC3	4.781	3.138
S2TC1	5.972	3.662
S2TC2	7.032	3.151
S2TC3	4.013	2.648
S3TC1	6.965	3.313
S3TC2	7.806	3.052
S3TC3	1.078	0.520

TABLE 26

TUKEY TEST DATA FOR COMPARISON OF SURFACTANTS
AND TARGET COMPOUNDS (HYPOTHESIS 2)

	Pairwise Mean Differences								
Variables	S1TC1	S1TC2	S1TC3	S2TC1	S2TC2	S2TC3	S3TC1	S3TC2	S3TC3
S1TC1	0.000								
S1TC2	-1.798	0.000							
S1TC3	-3.211	-1.413	0.000						
S2TC1	-2.019	*-0.222	1.191	0.000					
S2TC2	-0.959	0.839	2.252	1.061	0.000				
S2TC3	-3.979	-2.181	-0.768	-1.959	-3.020	0.000			
S3TC1	-1.026	0.771	2.184	0.993	*-0.068	2.952	0.000		
S3TC2	*-0.185	1.612	3.025	1.834	0.773	3.793	0.841	0.000	
S3TC3	-6.913	-5.116	-3.703	-4.894	-5.955	-2.935	-5.887	-6.728	0.000

* Not Significant at $P < 0.05$

TABLE 27

MEANS AND STANDARD DEVIATIONS FOR SURFACTANTS AND TARGET COMPOUND CONCENTRATIONS (HYPOTHESIS 3)

Variables	Mean	SD
S1TCC1	3.562	0.752
S1TCC2	5.954	2.289
S1TCC3	9.451	3.182
S2TCC1	2.804	0.976
S2TCC2	5.213	2.596
S2TCC3	9.002	2.765
S3TCC1	2.863	1.440
S3TCC2	4.885	3.030
S3TCC3	8.102	4.731

TABLE 28

TUKEY TEST DATA FOR COMPARISON OF SURFACTANTS AND TARGET COMPOUND CONCENTRATIONS (HYPOTHESIS 3)

Pairwise Mean Differences

Variables	S1TCC1	S1TCC2	S1TCC3	S2TCC1	S2TCC2	S2TCC3	S3TCC1	S3TCC2	S3TCC3
S1TCC1	0.000								
S1TCC2	2.392	0.000							
S1TCC3	5.889	3.497	0.000						
S2TCC1	-0.758	-3.015	-6.647	0.000					
S2TCC2	1.651	-0.741	-4.238	2.409	0.000				
S2TCC3	5.440	3.048	*-0.045	6.198	3.789	0.000			
S3TCC1	*-0.699	-3.091	-6.588	*0.059	-2.350	-6.139	0.000		
S3TCC2	1.323	-1.068	-4.565	2.082	*-0.327	-4.116	2.023	0.000	
S3TCC3	4.540	2.148	-1.349	5.298	2.889	-0.900	5.239	3.216	0.000

* Not Significant at $P < 0.05$

TABLE 29

MEANS AND STANDARD DEVIATIONS FOR TARGET COMPOUNDS AND TARGET COMPOUND CONCENTRATIONS (HYPOTHESIS 4)

Variable	Mean	SD
TC1TCC1	3.126	0.758
TC1TCC2	6.690	2.131
TC1TCC3	11.126	1.673
TC2TCC1	3.811	0.591
TC2TCC2	6.834	0.910
TC2TCC3	10.387	1.472
TC3TCC1	2.291	1.361
TC3TCC2	2.527	2.068
TC3TCC3	5.054	3.739

TABLE 30

TUKEY TEST DATA FOR COMPARISON OF TARGET COMPOUNDS AND TARGET COMPOUND CONCENTRATIONS (HYPOTHESIS 4)

	Pairwise Mean Differences								
Variables	TC1 TCC1	TC1 TCC2	TC1 TCC3	TC2 TCC1	TC2 TCC2	TC2 TCC3	TC3 TCC1	TC3 TCC2	TC3 TCC3
TC1TCC1	0.000								
TC1TCC2	3.564	0.000							
TC1TCC3	7.987	4.422	0.000						
TC2TCC1	*0.686	-2.879	-7.301	0.000					
TC2TCC2	3.708	*0.144	-4.278	3.023	0.000				
TC2TCC3	7.261	3.697	-0.725	6.576	3.553	0.000			
TC3TCC1	-0.835	-4.399	-8.822	-1.521	-4.543	-8.096	0.000		
TC3TCC2	*-0.599	-4.163	-8.586	-1.284	-4.307	-7.860	*0.236	0.000	
TC3TCC3	1.928	-1.636	-6.058	1.243	-1.780	-5.333	2.763	2.527	0.000

* Not Significant at $P > 0.05$

TABLE 31

MEANS AND STANDARD DEVIATIONS FOR SURFACTANTS AND SURFACTANT CONCENTRATIONS (HYPOTHESIS 5)

Variable	Mean	SD
S1SC1	5.091	3.047
S1SC2	6.540	3.297
S1SC3	7.335	3.304
S2SC1	5.039	3.424
S2SC2	5.878	3.493
S2SC3	6.121	3.248
S3SC1	4.982	4.034
S3SC2	5.286	3.978
S3SC3	5.582	3.936

TABLE 32

ANALYSIS OF VARIANCE COMPARING SURFACTANT CONCENTRATIONS, TARGET COMPOUND CONCENTRATIONS AND PHS (HYPOTHESIS 6)

Source	SS	df	MS	F	P
SC	213.396	2	106.698	14.874	0.000
TCC	4113.477	2	2056.739	286.708	0.000
pH	25.660	2	12.830	1.788	0.168
SC * TC	58.333	4	14.583	2.033	0.088
SC * pH	6.468	4	1.617	0.225	0.924
TCC * pH	2.795	4	0.699	0.097	0.983
SC * TCC* pH	3.742	8	0.468	0.065	1.000
Error	5035.892	702			

TABLE 33

MEANS AND STANDARD DEVIATIONS FOR SURFACTANTS AND PHS (HYPOTHESIS 6)

Variables	Mean	SD
S1pH1	6.317	3.343
S1pH2	6.402	3.366
S1pH3	6.247	3.342
S2pH1	5.795	3.264
S2pH2	6.116	3.655
S2pH3	5.107	3.249
S3pH1	5.341	4.058
S3pH2	5.345	4.041
S3pH3	5.164	3.967

TABLE 34

MEANS AND STANDARD DEVIATIONS FOR
TARGET COMPOUNDS AND PHS
(HYPOTHESIS 6)

Variables	Mean	SD
TC1pH1	7.058	3.602
TC1pH2	7.120	3.980
TC1pH3	6.751	3.382
TC2pH1	7.062	2.867
TC2pH2	7.159	2.826
TC2pH3	6.812	3.002
TC3pH1	3.333	2.866
TC3pH2	3.584	3.044
TC3pH3	2.955	2.681

TABLE 35

MEANS AND STANDARD DEVIATIONS FOR TARGET COMPOUND CONCENTRATIONS AND PHS (HYPOTHESIS 6)

Variables	Mean	SD
TCC1pH1	3.178	1.087
TCC1pH2	3.203	1.164
TCC1pH3	2.845	1.156
TCC2pH1	5.304	2.513
TCC2pH2	5.594	3.001
TCC2pH3	5.154	2.519
TCC3pH1	8.972	3.727
TCC3pH2	9.066	3.697
TCC3pH3	8.517	3.658

TABLE 36

ANALYSIS OF VARIANCE COMPARING SURFACTANT CONCENTRATIONS, TARGET COMPOUND CONCENTRATIONS AND BRINES (HYPOTHESIS 7)

Source	SS	df	MS	F	P
SC	213.396	2	106.698	14.874	0.000
TCC	4113.477	2	2056.739	286.708	0.000
B	0.524	2	0.262	0.036	0.964
SC * TCC	58.333	4	14.583	2.033	0.088
SC * B	4.544	4	1.136	0.158	0.960
TCC * B	2.710	4	0.677	0.094	0.984
SC * TCC * B	6.613	8	0.827	0.115	0.999
Error	5060.166	702	7.208		

TABLE 37

MEANS AND STANDARD DEVIATIONS FOR BRINES AND SURFACTANTS (HYPOTHESIS 7)

Variables	Mean	SD
S1B1	6.342	3.158
S1B2	6.309	3.332
S1B3	6.315	3.552
S2B1	5.770	3.302
S2B2	5.619	3.691
S2B3	5.629	3.251
S3B1	5.280	4.043
S3B2	5.297	3.988
S3B3	5.273	3.940

TABLE 38

MEANS AND STANDARD DEVIATIONS FOR BRINES AND TARGET COMPOUNDS (HYPOTHESIS 7)

Variables	Mean	SD
TC1B1	6.967	3.529
TC1B2	7.043	3.876
TC1B3	6.921	3.584
TC2B1	7.092	2.841
TC2B2	6.981	2.912
TC2B3	6.960	2.954
TC3B1	3.333	2.834
TC3B2	3.204	2.810
TC3B3	3.335	2.987

TABLE 39

MEANS AND STANDARD DEVIATIONS FOR TARGET COMPOUND CONCENTRATIONS AND BRINES (HYPOTHESIS 7)

Variables	Mean	SD
TCC1B1	3.165	1.161
TCC1B2	3.064	1.186
TCC1B3	2.999	1.088
TCC2B1	5.380	2.533
TCC2B2	5.399	3.010
TCC2B3	5.273	2.505
TCC3B1	8.847	3.663
TCC3B2	8.762	3.755
TCC3B3	8.945	3.685

TABLE 40

ANALYSIS OF VARIANCE COMPARING TYPES, TARGET COMPOUNDS AND TARGET COMPOUND CONCENTRATIONS (HYPOTHESIS 8)

Source	SS	df	MS	F	P
T	2345.079	1	2345.079	14.874	0.000
TC	7004.785	2	3502.393	286.708	0.000
TCC	5488.991	2	2744.495	0.036	0.000
T * TC	1781.125	4	890.563	2.033	0.000
T * TCC	277.798	4	138.899	0.158	0.000
TC * TCC	1310.039	4	327.510	0.094	0.000
T * TC * TCC	287.916	4	71.979	0.115	0.000
Error	3388.497	1440	2.353		

TABLE 41

TUKEY TEST DATA FOR COMPARISON OF TYPES AND TARGET COMPOUNDS (HYPOTHESIS 8)

Pairwise Mean Differences

Variables	T1TC1	T1TC2	T1TC3	T2TC1	T2TC2	T2TC3
T1TC1	0.000					
T1TC2	*0.035	0.000				
T1TC3	-3.686	-3.720	0.000			
T2TC1	-5.016	-5.051	-1.331	0.000		
T2TC2	*0.387	*0.352	4.072	5.403	0.000	
T2TC3	-6.631	-6.665	-2.945	-1.614	-7.017	0.000

* Not Significant at $P < 0.05$

TABLE 42

TUKEY TEST DATA FOR COMPARISON OF TYPES AND TARGET COMPOUND CONCENTRATIONS (HYPOTHESIS 8)

	Pairwise Mean Differences					
Variables	T1TCC1	T1TCC2	T1TCC3	T2TCC1	T2TCC2	T2TCC3
T1TCC1	0.000					
T1TCC2	2.274	0.000				
T1TCC3	5.775	3.501	0.000			
T2TCC1	-1.606	-3.881	-7.381	0.000		
T2TCC2	*-0.024	-2.299	-5.800	1.582	0.000	
T2TCC3	2.071	*-0.204	-3.705	3.677	2.095	0.000

* Not Significant at $P < 0.05$

TABLE 43

ANALYSIS OF VARIANCE COMPARING TYPES, TARGET COMPOUNDS AND TARGET COMPOUND CONCENTRATIONS (HYPOTHESIS 8)

Source	SS	df	MS	F	P
T	2345.079	1	2345.079	173.392	0.000
B	14.795	2	7.397	0.547	0.579
pH	13.207	2	6.604	0.488	0.614
T * B	8.086	4	4.043	0.299	0.742
T * pH	14.473	4	7.237	0.535	0.586
B * pH	10.013	4	2.503	0.185	0.946
T * B * pH	2.944	8	0.736	0.054	0.994
Error	19475.634	1440	13.525		

TABLE 44

MEANS AND STANDARD DEVIATIONS FOR SURFACTANT CONCENTRATIONS AND TARGET COMPOUNDS

Variables	Mean	SD
SC1TC1	6.283	3.132
SC1TC2	7.188	2.928
SC1TC3	1.641	0.987
SC2TC1	7.479	3.993
SC2TC2	6.972	2.876
SC2TC3	3.252	2.167
SC3TC1	7.167	3.715
SC3TC2	6.873	2.896
SC3TC3	4.979	3.681

TABLE 45

TUKEY TEST DATA FOR COMPARISON OF SURFACTANT CONCENTRATIONS AND TARGET COMPOUND CONCENTRATIONS

	Pairwise Mean Differences								
Variables	SC1TC1	SC1TC2	SC1TC3	SC2TC1	SC2TC2	SC2TC3	SC3TC1	SC3TC2	SC3TC3
SC1TC1	0.000								
SC1TC2	*0.905	0.000							
SC1TC3	-4.641	-5.547	0.000						
SC2TC1	*1.197	*0.291	5.838	0.000					
SC2TC2	*0.690	*-0.215	5.331	*-0.507	0.000				
SC2TC3	-3.030	-3.936	*1.611	-4.227	-3.720	0.000			
SC3TC1	*0.885	*-0.021	5.526	*-0.312	*0.195	3.915	0.000		
SC3TC2	*0.590	*-0.315	5.231	*-0.607	*-0.100	3.620	*-0.294	0.000	
SC3TC3	*-1.304	-2.209	3.338	-2.501	-1.994	*1.726	-2.188	-1.894	0.000

* Not Significant at $P < 0.05$

TABLE 46

MEANS AND STANDARD DEVIATIONS FOR SURFACTANTS, TARGET COMPOUNDS AND TARGET COMPOUND CONCENTRATIONS INTERACTIONS

Variables			Mean	SD
S1	TC1	TCC1	3.654	0.322
		TCC2	8.136	1.024
		TCC3	12.184	1.935
	TC2	TCC1	3.815	0.435
		TCC2	5.922	0.600
		TCC3	8.844	0.859
	TC3	TCC1	3.216	1.116
		TCC2	3.803	2.227
		TCC3	7.323	3.720
S2	TC1	TCC1	2.268	0.605
		TCC2	5.664	2.972
		TCC3	9.985	1.002
	TC2	TCC1	3.424	0.728
		TCC2	6.952	0.783
		TCC3	10.722	1.320
	TC3	TCC1	2.718	1.152
		TCC2	3.021	1.716
		TCC3	6.299	3.020

TABLE 46 (Continued)

Variables			Mean	SD
S3	TC1	TCC1	3.455	0.363
		TCC2	6.271	0.808
		TCC3	11.169	1.160
	TC2	TCC1	4.195	0.214
		TCC2	7.628	0.197
		TCC3	11.596	0.290
	TC3	TCC1	0.938	0.387
		TCC2	0.756	0.225
		TCC3	1.540	0.532

TABLE 47

TUKEY TEST DATA FOR SURFACTANTS, TARGET COMPOUNDS AND TARGET COMPOUND CONCENTRATIONS - PAIRWISE MEAN DIFFERENCES

		S1 TC1 TCC1	TC1 TCC2	TC1 TCC3	TC2 TCC1	TC2 TCC2	TC2 TCC3	TC3 TCC1	TC3 TCC2	TC3 TCC3	S2 TC1 TCC1	TC1 TCC2	TC1 TCC3	TC2 TCC1	TC2 TCC2	TC2 TCC3	TC3 TCC1	TC3 TCC2	TC3 TCC3	S3 TC1 TCC1	TC1 TCC2	TC1 TCC3	TC2 TCC1	TC2 TCC2	TC2 TCC3	TC3 TCC1	TC3 TCC2	TC3 TCC3
S1																												
TC1	TCC1	0.00	4.48	8.53	0.16	2.27	5.19	0.44	0.15	3.67	1.39	2.01	6.33	0.23	3.30	7.07	0.94	0.63	2.64	0.20	2.62	7.51	0.54	3.97	7.94	2.72	2.90	2.11
TC1	TCC2		0.00	4.05	4.32	2.14	0.71	4.92	4.33	0.81	5.87	2.47	1.85	4.71	1.18	2.59	5.42	5.11	1.84	4.68	1.86	3.03	3.94	0.51	3.46	7.20	7.38	6.60
TC1	TCC3			0.00	8.37	6.26	3.34	8.97	8.38	4.86	9.92	6.25	2.20	8.76	5.23	1.46	9.47	9.16	5.89	8.73	5.91	1.02	7.99	4.56	0.59	11.25	11.43	10.64
TC2	TCC1				0.00	2.11	5.03	0.60	0.01	3.50	1.55	1.85	6.17	0.39	3.14	6.91	1.10	0.79	2.48	0.36	2.46	7.35	0.38	3.81	7.78	2.88	3.06	2.27
TC2	TCC2					0.00	2.92	2.71	2.12	1.40	3.65	0.26	4.06	2.50	1.03	4.80	3.20	2.90	0.38	2.47	0.35	5.25	1.73	1.71	5.67	4.98	5.17	4.38
TC2	TCC3						0.00	5.63	5.04	1.52	6.58	3.18	1.14	5.42	1.89	1.88	6.12	5.82	2.55	5.39	2.57	2.32	4.65	1.22	2.75	7.91	8.09	7.30
TC3	TCC1							0.00	0.59	4.11	0.95	2.45	6.77	0.21	3.74	7.51	0.50	0.19	3.08	0.24	3.05	7.95	0.98	4.41	8.38	2.28	2.46	1.68
TC3	TCC2								0.00	3.52	1.54	1.86	6.18	0.38	3.15	6.92	1.08	0.78	2.50	0.35	2.47	7.37	0.39	3.83	7.79	2.87	3.05	2.26
TC3	TCC3									0.00	5.06	1.66	2.66	3.90	0.37	3.40	4.60	4.30	1.02	3.87	1.05	3.85	3.13	0.31	4.27	6.39	6.57	5.78
S2																												
TC1	TCC1										0.00	3.40	7.72	1.16	4.68	8.45	0.45	0.75	4.03	1.19	4.00	8.90	1.93	5.36	9.33	1.33	1.51	0.73
TC1	TCC2											0.00	4.32	2.24	1.29	5.06	2.95	2.64	0.63	2.21	0.61	5.50	1.47	1.96	5.93	4.72	4.91	4.12
TC1	TCC3												0.00	6.65	3.03	0.74	7.27	6.96	3.96	6.53	3.71	1.18	5.79	2.36	1.61	9.05	9.23	8.44
TC2	TCC1													0.00	3.53	7.30	0.71	0.40	2.87	0.03	2.85	7.74	0.77	4.20	8.17	2.49	2.67	1.88
TC2	TCC2														0.00	3.77	4.23	3.93	0.65	3.50	0.68	4.22	2.76	0.68	4.64	6.01	6.20	5.41
TC2	TCC3															0.00	8.00	7.70	4.42	7.27	4.45	0.45	6.53	3.09	0.87	9.78	9.97	9.18
TC3	TCC1																0.00	0.03	3.58	0.74	3.55	8.45	1.48	4.91	8.88	1.78	1.96	1.18
TC3	TCC2																	0.00	3.28	0.43	3.25	8.15	1.17	4.61	8.57	2.05	2.27	1.48
TC3	TCC3																		0.00	2.84	0.03	4.87	2.10	1.33	5.30	5.36	5.54	4.75
S3																												
TC1	TCC1																			0.00	2.82	7.71	0.74	4.17	8.14	2.52	2.70	1.91
TC1	TCC2																				0.00	4.90	2.08	1.36	5.32	5.33	5.51	4.73
TC1	TCC3																					0.00	6.97	3.54	0.43	10.23	10.41	9.63
TC2	TCC1																						0.00	3.43	7.40	3.26	3.44	2.65
TC2	TCC2																							0.00	3.97	6.69	6.87	6.09
TC2	TCC3																								0.00	10.66	10.84	10.06
TC3	TCC1																									0.00	0.18	0.60
TC3	TCC2																										0.00	0.78
TC3	TCC3																											0.00

TABLE 48

TUKEY TEST DATA FOR SURFACTANTS, TARGET COMPOUNDS AND TARGET COMPOUND CONCENTRATIONS - PROBABILITIES

		S1 TC1 TCC1	TC1 TCC2	TC1 TCC3	TC2 TCC1	TC2 TCC2	TC2 TCC3	TC3 TCC1	TC3 TCC2	TC3 TCC3	S2 TC1 TCC1	TC1 TCC2	TC1 TCC3	TC2 TCC1	TC2 TCC2	TC2 TCC3	TC3 TCC1	TC3 TCC2	TC3 TCC3	S3 TC1 TCC1	TC1 TCC2	TC1 TCC3	TC2 TCC1	TC2 TCC2	TC2 TCC3	TC3 TCC1	TC3 TCC2	TC3 TCC3
S1																												
TC1	TCC1	0.00	S	S	NS	S	S	NS	NS	S	NS	S	S	NS	S	S	NS	NS	S	NS	S	S	NS	S	S	S	S	S
TC1	TCC2		0.00	S	S	S	NS	S	S	NS	S	S	S	S	NS	S	S	S	S	S	S	S	S	NS	S	S	S	S
TC1	TCC3			0.00	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	NS	S	S	S	S	S	S
TC2	TCC1				0.00	S	S	NS	NS	S	S	S	S	NS	S	S	NS	NS	S	NS	S	S	NS	S	S	S	S	S
TC2	TCC2					0.00	S	S	S	NS	S	NS	S	S	NS	S	S	S	NS	S	NS	S	S	S	S	S	S	S
TC2	TCC3						0.00	S	S	S	S	S	NS	S	S	S	S	S	S	S	S	S	S	NS	S	S	S	S	S
TC3	TCC1							0.00	NS	S	NS	S	S	NS	S	S	NS	NS	S	NS	S	S	NS	S	S	S	S	S
TC3	TCC2								0.00	S	S	S	S	S	S	S	NS	NS	S	S	S	S	NS	S	S	S	S	S
TC3	TCC3									0.00	S	S	S	3.90	NS	S	S	S	NS	S	NS	S	S	NS	S	S	S	S	S
S2																												
TC1	TCC1										0	S	S	NS	S	S	NS	NS	S	NS	S	S	S	S	S	NS	S	NS
TC1	TCC2											0.00	S	S	NS	S	S	S	NS	S	NS	S	S	S	S	S	S	S	S
TC1	TCC3												0.00	S	S	NS	S	S	S	S	S	NS	S	S	S	S	S	S	S
TC2	TCC1													0.00	S	S	NS	NS	S	NS	S	S	NS	S	S	S	S	S	S
TC2	TCC2														0.00	S	S	S	NS	S	NS	S	S	NS	S	S	S	S	S
TC2	TCC3															0.00	S	S	S	S	S	NS	S	S	NS	S	S	S	S
TC3	TCC1																0.00	NS	S	NS	S	S	S	S	S	S	S	S	NS
TC3	TCC2																	0.00	S	NS	S	S	NS	S	S	S	S	S	S
TC3	TCC3																		0.00	S	NS	S	S	NS	S	S	S	S	S
S3																												
TC1	TCC1																			0.00	SS	S	NS	S	S	S	S	S
TC1	TCC2																				0.00	S	S	NS	S	S	S	S
TC1	TCC3																					0.00	S	S	NS	S	S	S
TC2	TCC1																						0.00	S	S	S	S	S
TC2	TCC2																							0.00	S	S	S	S
TC2	TCC3																								0.00	S	S	S
TC3	TCC1																									0.00	NS	NS
TC3	TCC2																										0.00	NS
TC3	TCC3																											0.00

S = Significant at P < 0.05
NS = Not Significant at P < 0.05

TABLE 49

MEANS AND STANDARD DEVIATIONS FOR TYPES, TARGET COMPOUNDS AND TARGET COMPOUND CONCENTRATIONS INTERACTIONS

Variables			Mean	SD
T1	TC1	TCC1	3.126	0.758
		TCC2	6.690	2.131
		TCC3	11.112	1.673
	TC2	TCC1	3.811	0.591
		TCC2	6.834	0.910
		TCC3	10.387	1.472
	TC3	TCC1	2.291	1.361
		TCC2	2.527	2.068
		TCC3	5.054	3.739
T2	TC1	TCC1	0.388	0.236
		TCC2	1.431	1.303
		TCC3	4.061	2.367
	TC2	TCC1	3.876	0.368
		TCC2	7.225	0.426
		TCC3	10.987	1.339
	TC3	TCC1	0.146	0.018
		TCC2	0.499	1.231
		TCC3	0.392	0.061

TABLE 50

TUKEY TEST DATA FOR TYPES, TARGET COMPOUNDS AND TARGET COMPOUND CONCENTRATIONS - PAIRWISE MEAN DIFFERENCES

		T1 TC1 TCC1	T1 TC1 TCC2	T1 TC1 TCC3	T1 TC2 TCC1	T1 TC2 TCC2	T1 TC2 TCC3	T1 TC3 TCC1	T1 TC3 TCC2	T1 TC3 TCC3	T2 TC1 TCC1	T2 TC1 TCC2	T2 TC1 TCC3	T2 TC2 TCC1	T2 TC2 TCC2	T2 TC2 TCC3	T2 TC3 TCC1	T2 TC3 TCC2	T2 TC3 TCC3
T1																			
TC1	TCC1	0.00	3.56	7.99	0.69	3.71	7.26	0.84	0.60	1.93	2.74	1.70	0.94	0.75	4.10	7.86	2.98	2.63	2.73
TC1	TCC2		0.00	4.42	2.88	0.14	3.70	4.40	4.16	1.63	6.30	5.26	2.63	2.81	0.53	4.29	6.54	6.19	6.30
TC1	TCC3			0.00	7.30	4.28	0.73	8.82	8.58	6.05	10.72	9.68	7.05	7.23	3.89	0.13	10.97	10.61	10.72
TC2	TCC1				0.00	3.02	6.85	1.52	1.28	1.24	3.42	2.38	0.25	0.06	3.41	7.18	3.67	3.31	3.42
TC2	TCC2					0.00	3.55	4.54	4.31	1.78	6.45	5.40	2.77	2.96	0.39	4.15	6.69	6.34	6.44
TC2	TCC3						0.00	8.10	7.86	5.33	10.00	8.96	6.33	6.51	3.16	0.60	10.24	9.89	10.00
TC3	TCC1							0.00	0.24	2.76	1.90	0.86	1.77	1.59	4.93	8.70	2.15	1.79	1.90
TC3	TCC2								0.00	2.53	2.14	1.09	1.53	1.35	4.70	8.46	2.38	2.03	2.14
TC3	TCC3									0.00	4.67	3.32	0.99	1.18	2.17	5.93	4.91	4.56	4.66
T2																			
TC1	TCC1										0.00	1.04	3.67	3.49	6.84	10.60	0.24	0.11	0.00
TC1	TCC2											0.00	2.63	2.45	5.79	9.56	1.29	0.93	1.04
TC1	TCC3												0.00	0.18	3.16	6.93	3.92	3.56	3.67
TC2	TCC1													0.00	3.35	7.11	3.73	3.38	3.48
TC2	TCC2														0.00	3.76	7.08	6.73	6.83
TC2	TCC3															0.00	10.84	10.49	10.60
TC3	TCC1																0.00	0.35	0.25
TC3	TCC2																	0.00	0.11
TC3	TCC3																		0.00

TABLE 51

TUKEY TEST DATA FOR TYPES, TARGET COMPOUNS AND TARGET COMPOUND CONCENTRATIONS - PROBABILITIES

		T1 TC1 TCC1	T1 TC1 TCC2	T1 TC1 TCC3	T1 TC2 TCC1	T1 TC2 TCC2	T1 TC2 TCC3	T1 TC3 TCC1	T1 TC3 TCC2	T1 TC3 TCC3	T2 TC1 TCC1	T2 TC1 TCC2	T2 TC1 TCC3	T2 TC2 TCC1	T2 TC2 TCC2	T2 TC2 TCC3	T2 TC3 TCC1	T2 TC3 TCC2	T2 TC3 TCC3
T1																			
TC1	TCC1	0.00	S	S	NS	S	S	NS	NS	S	S	S	NS	NS	S	S	S	S	S
TC1	TCC2		0.00	S	S	NS	S	S	S	S	S	S	S	S	NS	S	S	S	S
TC1	TCC3			0.00	S	S	NS	S	S	S	S	S	S	S	S	NS	S	S	S
TC2	TCC1				0.00	S	S	S	NS	NS	S	S	NS	NS	S	S	S	S	S
TC2	TCC2					0.00	S	S	S	S	S	S	S	S	NS	S	S	S	S
TC2	TCC3						0.00	S	S	S	S	S	S	S	S	NS	S	S	S
TC3	TCC1							0.00	NS	S	S	NS	S	S	S	S	S	S	S
TC3	TCC2								0.00	S	S	NS	S	S	S	S	S	S	S
TC3	TCC3									0.00	S	S	NS	NS	S	S	S	S	S
T2																			
TC1	TCC1										0.00	NS	S	S	S	S	NS	NS	NS
TC1	TCC2											0.00	S	S	S	S	NS	NS	NS
TC1	TCC3												0.00	NS	S	S	S	S	S
TC2	TCC1													0.00	S	S	S	S	S
TC2	TCC2														0.00	S	S	S	S
TC2	TCC3															0.00	S	S	S
TC3	TCC1																0.00	NS	NS
TC3	TCC2																	0.00	NS
TC3	TCC3																		0.00

S = Significant at P < 0.05
NS = Not Significant at P < 0.05

TABLE 52

STATISTICS FOR BLANKS

Variable	N*	Mean	SD
Entire Sample	727	0.223	0.094
S1	242	0.241	0.100
S2	243	0.221	0.087
S3	242	0.209	0.090
TC1	242	0.210	0.088
TC2	243	0.238	0.101
TC3	242	0.222	0.999

* Two blanks were lost in sample preparation

TABLE 53

ANALYSIS OF REPLICATES FOR EXPERIMENTAL BIAS

Source	SS	df	MS	F	P
Rep	0.618	2	0.309	0.022	0.978
Error	30525.342	2184	13.977		

VITA

Sarah Leigh Kimball

Candidate for the Degree of

Doctor of Philosophy

Thesis: THE INFLUENCE OF SELECTED SURFACTANTS AND WATER QUALITY PARAMETERS ON SURFACTANT-ENHANCED SOIL FLUSHING OF HYDROPHOBIC HYDROCARBON CONTAMINATED SOIL

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